REMARKS ON TESTING THE RELIABILITY OF IODINE ADSORPTION IN ION-EXCHANGING CHARCOAL-FILTERS WITH RESPECT TO SOLVENT LOADINGS

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Abstracts:

The reliability of high-efficient removal of fission iodine and its compounds depends on the condition of iodide-impregnated charcoal, especially on foreign loads, e.g. solvents. Samples of the charcoal taken from monitor-filters will have an equivalent load if flow-velocity is equal to that in the iodine-filter. But, the influence of geometric form and of bulk density is not to be neglected, insofar as conditions for identic flow-velocity cannot be assumed. It seems, that a good sample only can be taken directly out of the charcoal by pipette. Foreign loads below about 3% have practically no influence on the reliability of high-efficient-iodine-removal. When operating a charcoal-filter at temperatures in the range of 70°C to 90°C the equilibrium of adsorption of solvents is below this level with respect to the concentrations occuring in practice. Further advantages are: The relative humidity is lowered and the humidity of the carbon is lowered. Therefore the iodine-removal can be kept to a high efficiency.

Introduction:

One cause of failures in iodine removal with iodide impregnated ion-exchanging charcoal filters, here briefly called iodine-filters, is caused by foreign load on the charcoal, e.g. with solvents from painting or cleaning. This effect often is called poisoning or ageing of the charcoal. To ensure the reliability of iodine removal with the necessary high efficiency, the condition of the charcoal has to be checked at not too long intervals. Therefore samples of the charcoal are to be analized and their efficiency against methyl-iodide is tested. The problem is to get a good average sample. One solution for this task is to install parallel to the iodine-filter several monitor-filters with a small diameter and a depth of the bed equal to the depth of the bed of the iodine filter, filled with charcoal up to the same bulk density as the charcoal in the iodine-filter has (fig.1). If these requirements are fulfilled the flow velocities should be equal and correct informations on the

conditions of the charcoal is to be expected.

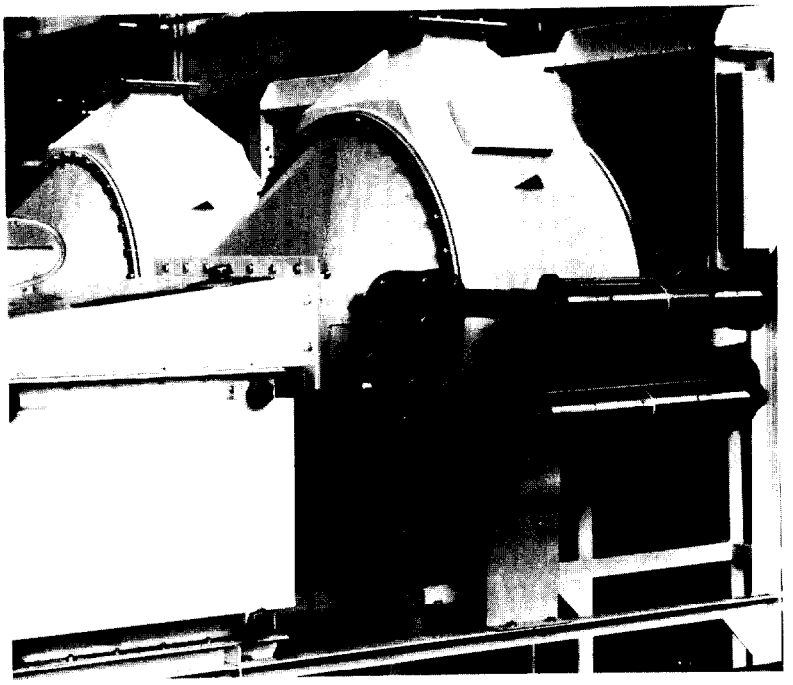

Fig. 1:
Iodine adsorption filter with deep-bed filter type KCR and 2 monitoring filters
(Courtesy Ceagfilter und Entstaubungstechnik Dortmund, BRD)

Influence of geometry, bulk density and pipe diameter on flow velocity

In practice the iodine filter is not a cylindrical vessel. Above there is a dome to fill the filter with charcoal and below there is a hopper to remove the charcoal.
Let us assume that the iodine-filter has a circular cross-section with a diameter D and an area A (fig. 2), then the pressure drop Δp at the airflow $\dot{V}$ may be written as

$$\Delta p = c \cdot \frac{\varrho}{2} \cdot \left(\frac{\dot{V}}{A}\right)^2 \qquad A = \frac{\pi \cdot D^2}{4} \qquad A' = \frac{\pi \cdot D}{4} \; (D + 2\,\delta D) \qquad (1)$$

where C stands for a resistance-coefficient and ϱ for the air-density. The dome and the hopper (fig. 3) give an enlargement of the cross-section of flow. Let us assume that this new cross-section becomes elliptic with

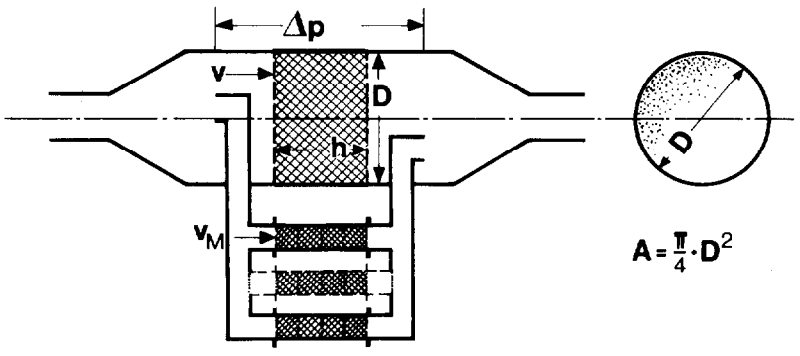

Fig. 2:
Iodine-filter with monitoring-filter; the deep-bed-vessel with circular cross-section (schematic drawing)

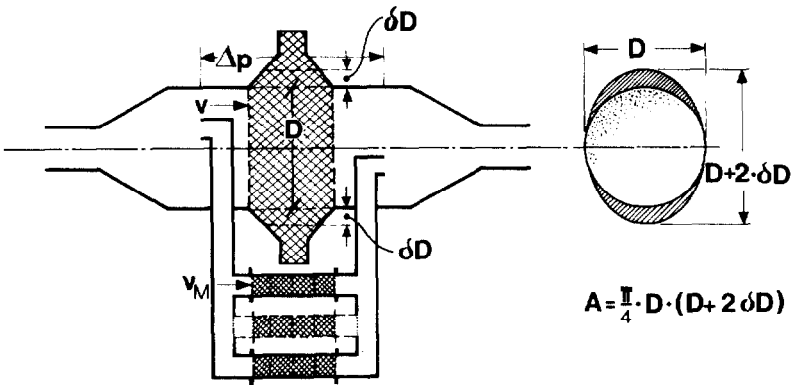

Fig. 3:
Iodine-filter with monitoring-filter; the deep-bed-vessel with dome and hopper and elliptical cross-section (schematic drawing)

the small axis D and the large axis (D+2δD), the new pressure-drop Δp' becomes

$$\Delta p' = \Delta p \left(\frac{1}{1+2\,\delta D/D}\right)^2 \sim \Delta p\left(1-4\,\frac{\delta D}{D}\right) \qquad (2)$$

(with $\delta D/D \ll 1$)

This pressure drop gives the acting force to drive a flow through the monitor-filters. The question is, what flow-rate will be caused by this pressure drop. To get an estimated figure, let us assume that flow and pressure drop are in accordance with the formula given by FEHLING (1), which is secured by experiment in the limits of Reynold's Number 15 < Re < 300. For a flow-velocity of $.5 m_S^{-1}$ and a charcoal-grain size of .003 m the Reynold's Number is about 30, so that the premise is fulfilled. The FEHLING formula gives a relationship between the acting pressure drop Δp, the coefficient of resistance of a single grain c_w, the mean diameter of the grain $\bar{a}_g$ and their shape-factor m, the depth of the bed L, the relative pore-volume of the bed Vp air-density ϱ and air-velocity w:

$$\Delta p = \frac{c_w \cdot m}{\bar{a}_g \cdot L} \cdot \frac{1}{Vp^4} \cdot \frac{\varrho}{2} w^2 \quad \text{(according to FEHLING /1/)} \qquad (3)$$

Or, for the air-velocity through the monitor filters (marked with the index M)

$$w_M = \sqrt{\frac{2\bar{a}_g\, L}{\varrho\, c_w{}^m}}\, Vp_{iM}^4 \sqrt{\Delta p'} \qquad (4)$$

with Δp' from (2) and Δp from (3) the ratio w_M/w is obtained

$$\frac{w_M}{w} = \sqrt{\frac{2\bar{a}_g\, L}{\varrho\, c_w{}^m}}\, Vp_{iM}^4 \sqrt{\frac{\varrho\, c_w{}^m}{2\bar{a}_g\, L}\,\frac{1}{Vp^4}} \sqrt{1-4\,\frac{\delta D}{D}} \qquad (5)$$

or

$$= \sqrt{\frac{Vp_{iM}^4}{Vp^4}} \sqrt{1-4\,\frac{\delta D}{D}} \sim \frac{Vp_{iM}^2}{Vp^2}\left(1-2\,\frac{\delta D}{D}\right) \qquad (6)$$

(with $\delta D/D \ll 1$)

FEHLING (1) studied further the influence of the wall, and he found that the pore-volume is to be corrected. His result is given by

$$Vp_{,M} = Vp_{,\infty}(1+8\,\frac{\overline{a_g}}{D_M}) \qquad (7a)$$

where Vp stands for the pore-volume of a charcoal-bed in a large vessel at the maximum packing density. The relationship between the pore-volume at maximum packing density and a pore-volume at lower packing density may be written as

$$Vp = Vp_{,\infty}\,(1+\frac{\delta Vp}{Vp}) \qquad (7b)$$

The formula (9a) is of importance for the monitoring-filter, due to their small diameter; (9b) gives the pore-volume with variations in the packing density. Therefore (9b) relates mainly to the iodine filter itself, because the packing density of the charcoal in the monitoring-filter can be kept near the attainable maximum, while the packing density of the iodine filter varies from charging to charging. Inserting (7a) and (7b) into (6) the ratio w_M/w becomes:

$$\frac{w_M}{w} = \frac{Vp_{,\infty}^2(1+8\,\frac{\overline{a_g}}{D_M})^2}{Vp_{,\infty}^2(1+\frac{\delta Vp}{Vp})^2}\,(1-2\,\frac{\delta D}{D}) \qquad (8)$$

or

$$\sim (1-2\,\frac{\delta Vp}{Vp})(1-2\,\frac{\delta D}{D})(1+16\,\frac{\overline{a_g}}{D_M}) \qquad (9)$$

(with $\delta Vp/Vp \ll 1$ and $\overline{a_g}/D_M \ll 1$)

In practice these correction numbers are in the following range:

$0 < \frac{\delta Vp}{Vp} < .2$ (bulk-density varies about 7%)

$0 < \frac{\delta D}{D} < .16$ (half height of dome and of hopper)

$\frac{16\,\bar{a}_g}{D_M} \sim .3$ (charcoal-grain-size about 1 mm, diameter of monitor-filter 50 mm)

With these correction numbers the ratio of flow-velocities goes to

$$.5 < \frac{w_M}{w} < 1.3$$

and the correction numbers are in the nature of systematic errors.

To examine this conclusion, experiments were carried out. The iodine-filter was a deep-bed filter of the KCR-type (fig. 1). The hollow space for the charcoal was 324 litres. This filter was charged with charcoal of cylindric grain with a diameter of 1.5 mm and a ratio between length and diameter of about 2 with a narrow distribution; it was charcoal of CEAG-type CB 1.5. The iodine-filter (with its monitoring filters) was installed in a loop and the air-flow through it was found by measuring the rotation speed of the blower (which had previously been calibrated), and by use of the blower characteristics.
Due to this, there is a hysteresis at low flow velocities, i.e. less than .35 m_s^{-1} ; this hysteresis may be caused by the effect of "rotating stall", but it does not influence the results which were taken by measuring the pressure drop at flow velocities above this critical limit.
The monitor-filters were tested in a separate test-device. The flow was measured by flow meters. The pressure drop itself was taken by static taps before and behind the filter under test and was measured with a water-gauge. Iodine-filter and monitor-filter were charged with practically identic charcoal up to the same depth of the bed. The packing-density at the monitor filter, which is easy to handle, was brought to the highest attainable level. The packing density of the charcoal in the iodine-filter was kept to a low level for the first run. After this, the packing density was increased by hammering. Due to this, up to about 7% of the volume of charcoal had to be filled up. Apart from this packing density the bed of charcoal in the iodine-filter and in the monitor-filter are to be assumed as identical.

The pressure drop flow velocity characteristic of the monitor-filter so charged is shown in fig. 4. The uncertainty is in the range of $\pm$ 10%. The pressure drop / flow-velocity-characteristic of the iodine-filter depends on the packing density and varies within the characteristics of "low-bulk-density" and high-bulk-density". The characteristics show that the pressure drop for a flow velocity of .5 m_s^{-1} may vary between 400 Pa m^{-1} and 540 Pa m^{-1}. This pressure drop drives the flow through the monitor-filter only with a velocity of .27 ms^{-1} to .34 ms^{-1}. The ratio w_M/w was found to be in the range of .55 to .68. This is in the lower range of the figures to be expected.

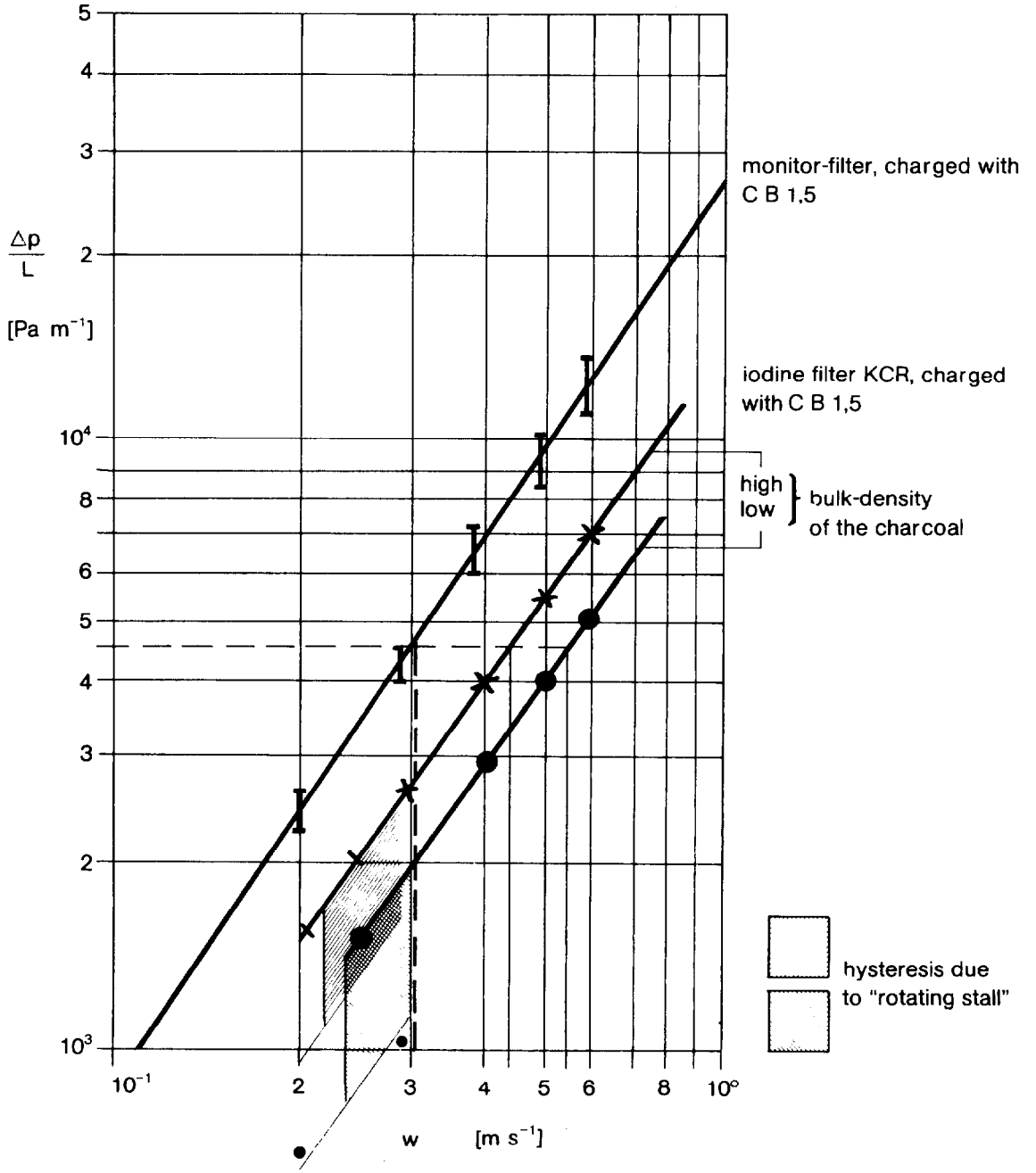

Fig. 4: Pressure drop / flow velocity characteristics of monitor filter and iodine filter type KCR

The use of charcoal with a wider distribution of the ratio length to diameter, or the use of broken charcoal will give a ratio of w_M/w still below the result obtained with this special type of cylindrical charcoal.

In addition to the studies of the relationship between pressure drop and flow velocity with respect to the packing density, efficiency tests against radio-active methyl-iodide are carried out. First results lead to the conclusion that the packing density (within the limits mentioned) has no remarkable influence on the methyl-iodide efficiency. A final report

of these studies is intended to be published later.

According to this it seems improbable that a ratio near 1 can be obtained and that good average samples can be got by taking charcoal from monitor filters.
Another solution for getting charcoal samples is independent on the flow and the influences mentioned on it. The samples are taken by pipette (fig. 5) direct from the bed. Therefore the pipette is inserted into the

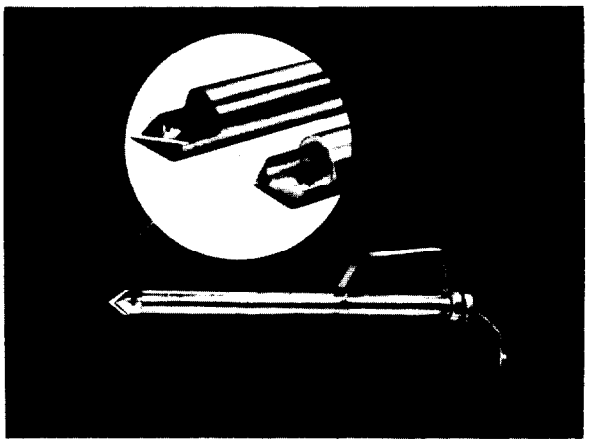

Fig. 5:
Pipette to get samples from the deep-bed (Courtesy Technische Universität Stuttgart Abteilung Mechanische Verfahrenstechnik, Stuttgart, BRD)

filter vessel and into the charcoal bed by means of guide bushes provided.

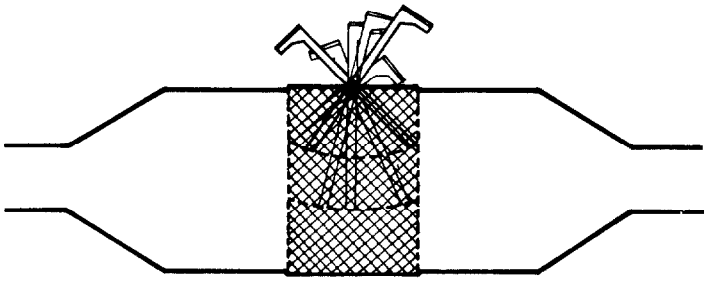

Fig. 6:
Pipette used to take samples from two different planes

If, for example, three samples are to be taken in two planes (fig. 6), the filter vessel should have a handhole, closed with a plate bearing the guide bushes, in this case six, fixed in the desired directions (or there may be one turnable and with adjustable groves for the different angles, under which the pipette is to be inserted).

In connection with the uncertainty of getting good average samples already mentioned by monitor filters, the question arises whether there is any possibility of preventing such foreign loadings and there are two possible solutions:

i : to remove the foreign impurities before they reach the iodine filter,

ii : to prevent the adsorption of these foreign impurities.

The first solution leads to prefilters (fig. 7).

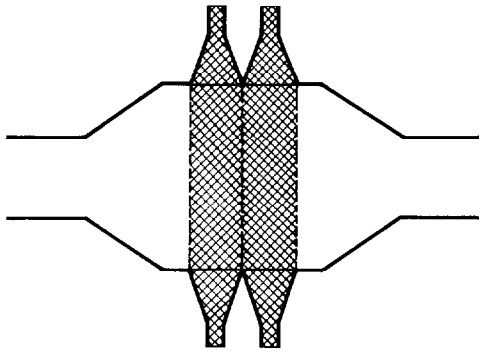

Fig. 7:
Deep-bed-filter with double layer: The first acts as prefilter, the second as iodine filter

But using adsorption-type prefilters, one has to remember that the amount of adsorbed matter depends on the vapour-pressure of this matter in the ambient air. If, some time after painting or cleaning, the vapour pressure drops to (or near to) 0, adsorbed matter will leave the charcoal, will be desorbed. Therefore the charcoal in the prefilter may get a peak charge of solvent but will not be a safe storage over a long time. In consequence the charcoal of the prefilter has to be changed in short intervals, but nobody knows the time at which a surge of organic matter e.g. from painting reaches the prefilter and what time is needed to lower the high loading in front of the prefilter and to distribute the load over prefilter and iodine filter. This problem may be solved by protection filters which act as prefilters during that time the air contains organic matter. This may be tested by infrared or ultra-violet spectroscopy, by flame photometery or by combustion analysis. These protection filters (fig. 8) are by-passed by a duct, which can be closed if foreign matter is detected.

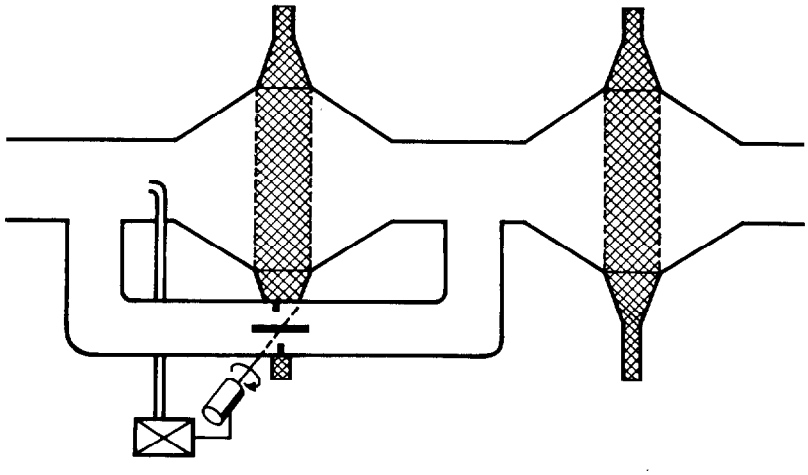

Fig. 8: Iodine-filter with by-passed protection-filter

DISCUSSION

DEITZ: Is the change in packing densities to be ascribed to particle breakdown or are we describing something due to the ordering of particles? Is there any way to sort this out?

STRAUSS: I think that the rise in packing density or the lowering of the pore-volume of the charcoal depends on the grains, which are, after filling, in randomly distributed directions. After hammering, they turn a little bit and they give a higher packing density.

DEITZ: But not particle breakdown?

STRAUSS: No, there is no particle breakdown. This has been checked in other connections. We are sure there is no particle breakdown.

WILHELM: There is another effect when you fill a big charcoal unit, as shown by Dr. Strauss. The pellets will have a horizontal orientation and the flow will be horizontal, too, i.e., parallel to grain layers. If you fill the bypass control filter vertically, the gas stream in the bypass filter flows perpendicular to the charcoal grain layers. In the case of pelletized charcoal and of charcoal in the form of little plates, this is a very important effect. When the charcoal is in horizontal layers and the air is coming down vertically, the canister has a much higher resistance than when flow is parallel to the particle layers. If you have little plates, you have the same effect.

PARISH: I would like to comment and also ask a question. First, I concur with the findings of Mr. Strauss. We have also evaluated the test canisters and have found that when proper consideration is not given to packing the adsorbent, the resultant test canister flow may be very nonrepresentative. However, when properly packed, we have repeatedly obtained very representative velocity through the canisters, varying from 8 per cent to minus 5 per cent relative to the main bed. I would like to ask if you would define for us what you mean when you say "hammer the large bed for packing purposes?"

STRAUSS: I agree fully with your remark. It is a problem to get good distribution, but one can do this by filling to the upper level and then bringing up the packing density with hammering. We fill up in this way with airflow to a point where the pressure drop becomes a constant value at rated flow.

RIVERS: The use of the canister is very convenient and gives you an easily obtainable sample, with which you can say whether the bed needs changing, for example, without doing anything to the main bed. Would it not be possible to make a shallower test canister which would then, of course, have less resistance and greater penetration than the main bed? At least it would be on the conservative side as a test device.

STRAUSS: If I understand you right, you want to keep canister

filters to check the main beds?

RIVERS: My canisters in parallel with the filter bed would have less depth and therefore less resistance and could be made to pass the same velocity as the main bed, but would last for less time than the main bed.

STRAUSS: But in normal cases, the difference in flow geometry and lower packing density in the main filter results in a lower relative velocity through the monitoring filter. Lowering the flow-resistance cannot solve this problem because our legislation forces us to use an identical bed.

AIRBORNE ELEMENTAL IODINE LOADING CAPACITIES OF METAL ZEOLITES AND A DRY METHOD FOR RECYCLING SILVER ZEOLITE*

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ABSTRACT

Several metal-exchanged zeolites have been tested to determine their elemental-iodine-loading capacities at breakthrough in air streams. The experiments were directed toward the application of the adsorbents for the removal of iodine-129 from the process off-gas of nuclear fuel reprocessing plants. The effects of the bed temperature, face velocity, bed depth, water vapor, and NO_2 on the loading capacities were examined. Only silver-exchanged zeolite was found to have a high chemisorption capacity for elemental iodine both in dynamic and static loading tests. The chemisorption capacities of lead-, cadmium-, and silver-exchanged zeolites for iodine are discussed in terms of thermodynamics.

Experiments were conducted to develop a method for recycling silver-exchanged zeolite. Iodine-desorption tests were performed by purging iodine-loaded silver-exchanged zeolite with pure hydrogen at bed temperatures of 400 to 700°C. The predicted rates of hydrogen iodide removal from silver iodide based on thermodynamic calculations are compared to the rates of removal observed from silver iodide dispersed in a zeolite matrix. The characteristics of test beds which were regenerated and reloaded several times are described. The use of lead-exchanged zeolite as an adsorbent for the hydrogen iodide purged from the silver-exchanged zeolite was studied. The potential application of silver-exchanged zeolite as a primary adsorbent for radioiodine removal from process off-gas and lead-exchanged zeolite as a secondary adsorbent for storage is evaluated.

INTRODUCTION

Fission-product iodine-129 is produced in nuclear power reactors and subsequently released as organic iodides and elemental iodine (I_2) into the process off-gas of reprocessing plants during fuel dissolution. Based on an iodine-129 content[1] of 40 mCi/MTU burned at 40,000 megawatt days and 90% volatilization of the iodine, it is estimated that as much as 330 kg/yr (54Ci) would be released from the stack gas of a 5 tonne/day reprocessing plant without the use of iodine-recovery systems. The proposed[2] EPA release limit could require at least 99.5% abatement of iodine-129 from the gaseous effluents (calculations are given in Appendix A). Even though the total release of iodine-129 would pose little concern on a world-wide scale, collection and storage will probably become necessary to avoid localized buildup in the environs of

*Work performed under USERDA Contract E-(10-1) 1375 S-72-1.

reprocessing plants.

Numerous low-loading tests (less than 10 mg iodine per gram substrate) have been run and decontamination factors (DF's) of 10^2 to 10^5 have been reported[3,4,5,6,7] for the removal of iodine from airstreams. However, very little data have been reported for long-term tests in which iodine-loading capacities at breakthrough were studied. For application of iodine-recovery systems to reprocessing plants, both high DF's and loading capacities will be necessary to minimize capital costs and the amount of waste generated. Pence, Duce and Maeck[3] found that silver-exchanged zeolite (AgX) would adsorb 84 mg of methyl iodide (CH_3I) per gram of AgX in dry air at 25°C with a DF>10^4. Ackley and Combs[7] reported a loading of 209 mg CH_3I/g AgX in air containing 3% water vapor at 200°C with a DF>100. At a DF of >10^4 their loading was about 87 mg CH_3I/g AgX. Wilhelm and Schüttelkopf[6] obtained loadings of about 40 mg I_2 or CH_3I per gram Ag-KTB for DF's>100 at bed temperatures of 150°C in the presence of 3% H_2O and 2.5% NO_2. The silver content of Ag-KTB is about 78 mg Ag/g Ag-KTB as compared to 360 mg Ag/g AgX. Collard and coworkers[8] reported a maximum loading of 52 mg I_2/g AgX at bed temperatures between 30 and 100°C. The DF and composition of the test gas were not given. To our knowledge, no systematic study of the effect of experimental variables on the iodine-loading capacity of silver-loaded adsorbents has been conducted. In our program, the effects of face velocity, bed depth, bed temperatures, water vapor and NO_2 on the elemental-iodine-loading capacity of AgX were studied.

It has been suggested[9] that lead-exchanged zeolite (PbX) might be used for elemental-iodine removal in place of AgX. Although data exist[3,7,10] which indicate that metal-exchanged zeolites (except AgX) generally have poor efficiences and/or low capacities for CH_3I removal, their efficiency for I_2 remains an open question. Pence and coworkers[4] indicated that high DF's with PbX were obtainable in dry-air streams and low loadings (about 1 mg I_2/g PbX) but that the efficiency was extremely poor at high relative humidity. Gal and coworkers[10] have indicated that partial chemisorption with CH_3I was observed on PbX and cadmium-exchanged zeolite (CdX) in static adsorption-desorption tests. In our program screening and loading tests were conducted on CdX, PbX, zinc- and copper-exchanged zeolites (ZnX, CuX) to determine if they would be potential adsorbents for elemental-iodine removal.

Because silver is a valuable resource, a method to regenerate spent AgX would improve the economic feasibility of adsorbent technology. Scoping studies on a dry method to regenerate and recycle spent AgX were conducted. In conjunction with this, PbX was used as a secondary adsorbent for the final collection and storage of iodine. The results of the comprehensive study on the adsorption characteristics of AgX, the screening tests on metal-exchanged zeolites, and the regeneration tests are discussed below. Application of adsorbent technology to reprocessing plants is also treated.

EXPERIMENTAL PROCEDURE

The metal-exchanged zeolites used in these studies were prepared by ion-exchange with 1.6 mm spheres of Linde Molecular Sieve Type 13X. Batch-exchange procedures were used in which the zeolite was contacted several times with a hot solution of the desired metal nitrate or acetate. The exchanged zeolites were washed with distilled water until excess cations were removed and dried by purging with dry air at 100°C. The extent of exchange was measured by dissolving samples in nitric acid and analyzing the amount of sodium which remained in the exchanged zeolites by flame-emission spectroscopy. Analysis indicated 99.9, 98, 92, 85, and 75% exchange for Ag^{+}, Pb^{++}, Cd^{++}, Cu^{++}, and Zn^{++} respectively.

Screening and iodine-loading tests were conducted using the apparatus illustrated in Figure 1. Heated-air streams containing desired amounts of water vapor, contaminant gases and airborne-elemental iodine tagged with iodine-131 were passed through the test beds. Iodine breakthrough was detected by passing an effluent slipstream through a small-adsorbent bed monitored by a gross-gamma counter. Silver-exchanged zeolite was used for backup beds. A Pyrex cylinder 5 cm in diameter was used for a test-bed holder. Up to 15-cm-bed depths could be tested and each 2.5-cm segment could be analyzed for its iodine content. A gamma spectrometer was used to determine the amount of iodine-131 in the test beds and based on the known ratios of iodine-127/iodine-131, the iodine loadings were obtained. Up to 60 g sources of tagged iodine were prepared by adding 10 mCi of iodine-131 to elemental iodine dissolved in diethyl ether. The solution was evaporated to dryness and the crystalline iodine was transferred in the vapor phase by a heated airstream into a condenser where it was recrystallized. Airborne iodine was introduced into the carrier gas by passing hot water through the outer jacket of the condenser and purging the crystalline iodine with helium. The experimental conditions used for testing are summarized in Table I.

Iodine-desorption tests were conducted using an apparatus which is illustrated in Figure 2. Silver-exchanged zeolite containing iodine (AgIX) was purged with pure hydrogen (H_2), and the desorbed hydrogen iodide (HI) was recovered downstream on PbX. During the desorption tests the effluent from the AgIX bed was sampled with a 10-cm-quartz-absorption cell and the absorbance by HI in the cell was measured with a UV-VIS spectrophotometer. The partial pressure of HI (P_{HI}) was obtained from the equation: $P_{HI} = A/ab$ where A = the measured absorbance, a = the molar absorbitivity (7.22 $atm^{-1}cm^{-1}$ at 21°C)[11] at 215 nm, and b = the path length (10 cm).

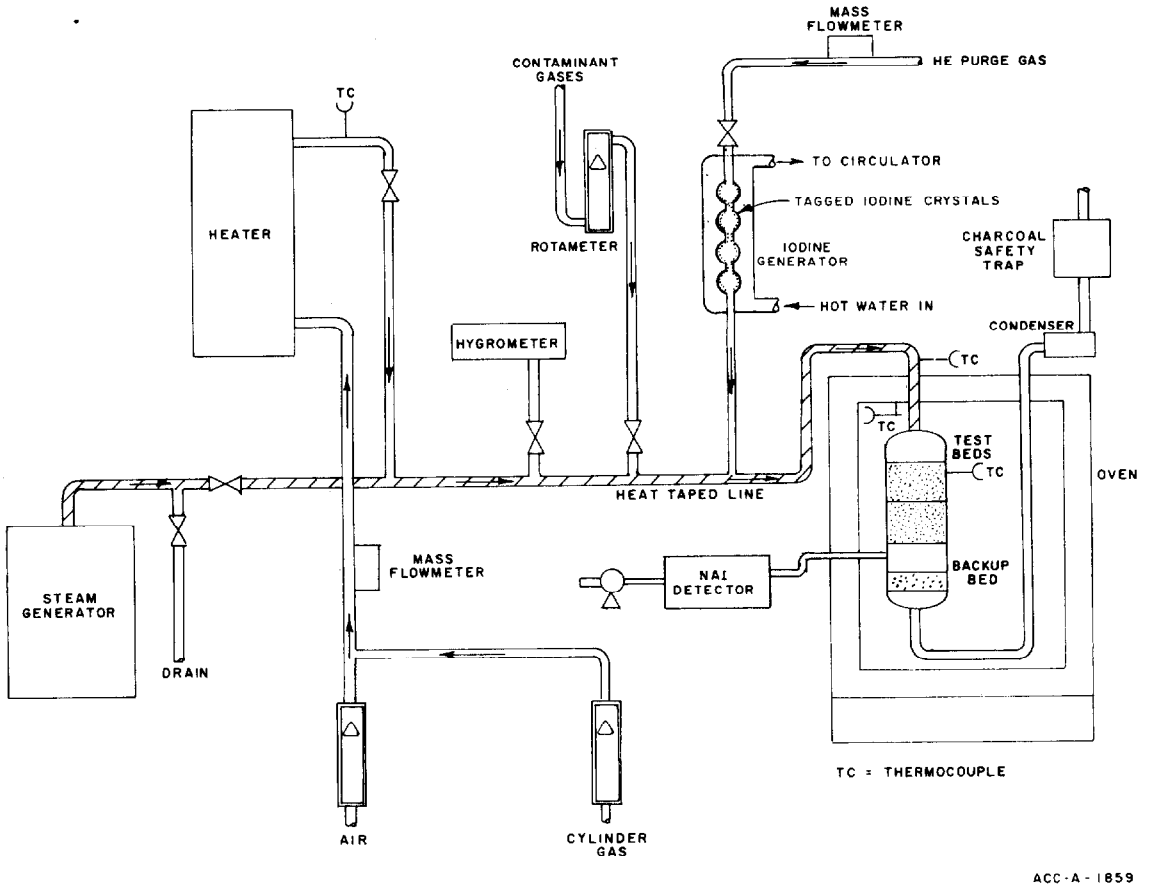


Figure 1. Test Apparatus for Iodine-Adsorption Studies

Table I

EXPERIMENTAL CONDITIONS

Experimental Variable	Screening Tests	Loading Tests
Dry-bed weight (g)	99	99, 198, 297
Bed diameter (cm)	5	5
Bed depth (cm)	5	5, 10, 15
Carrier gas	air	air
Superficial-face velocity at 25°C (m/min)	15	15, 30, 60
I_2 concentration (mg/m^3)	∿90	∿500
Loadings (mg I_2/g bed)	∿1.4	3.5 to 170
H_2O concentration (%)	0 to 10	0 and 5
NO_2 concentration (%)	0	0 and 2
Pretest purge (hr)	1	1
Test period (hr)	1	1 to 60
Post-test purge (hr)	0.25	20

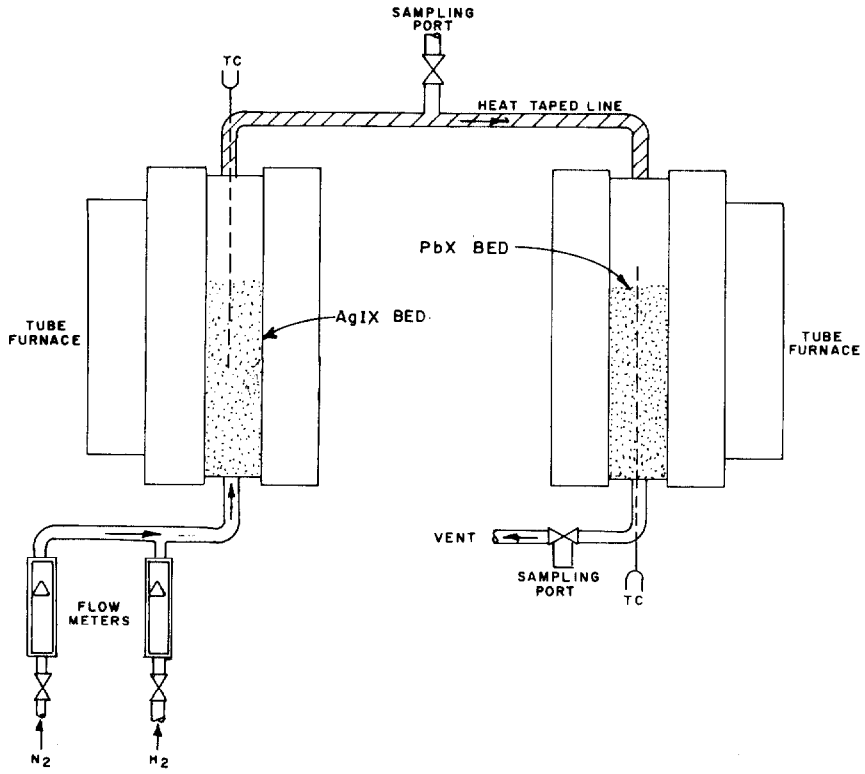


Figure 2. Test Apparatus for Iodine-Desorption Studies

EXPERIMENTAL RESULTS

Screening Tests

Several metal-exchanged zeolites were tested for the effect of cation, bed temperature, and water-vapor content on I_2 removal efficiency from air streams. The results are given in Table II.

Table II

SCREENING TESTS FOR 5-cm-DEEP BEDS

Adsorption Test Conditions (a)		I_2 Adsorption Efficiency (%)				
Water Vapor (%)	Bed Temp (°C)	CdX	NaX	PbX	ZnX	CuX
1.5	100	99.986	99.86	93.45	--	31.67
1.5	200	99.836	99.93	88.15	--	0.45
8.5	100	99.992	80.69	56.88	4.17	4.96
8.5	200	99.985	64.39	77.61	4.15	0.50

(a) Test conditions: 60-min-pretest purge, 60-min-test period, 15-min-post-test purge, 15 m/min face velocity, 90 mg I_2/m^3 airborne concentration, 1.4 mg I_2/g substrate loading at 99% efficiency.

The high efficiency of NaX in the presence of 1.5% water vapor indicates that considerable physical adsorption is taking place in the unexchanged substrate with the low loading used. The extremely low efficiencies observed for ZnX and CuX relative to NaX was unexpected and is not understood. Using the same test conditions as above, the test space for PbX and CdX was expanded to study the response surface for I_2 removal efficiency as a function of water-vapor content and bed temperature. The results are given in Figure 3. The response surface for CdX is almost flat in the region between 100 and 250°C with an average-adsorption efficiency of 99.82%. The efficiency appears to drop off sharply around 250°C. No trend is apparent with the PbX and except for one data point, iodine-adsorption efficiencies above 99% were not observed.

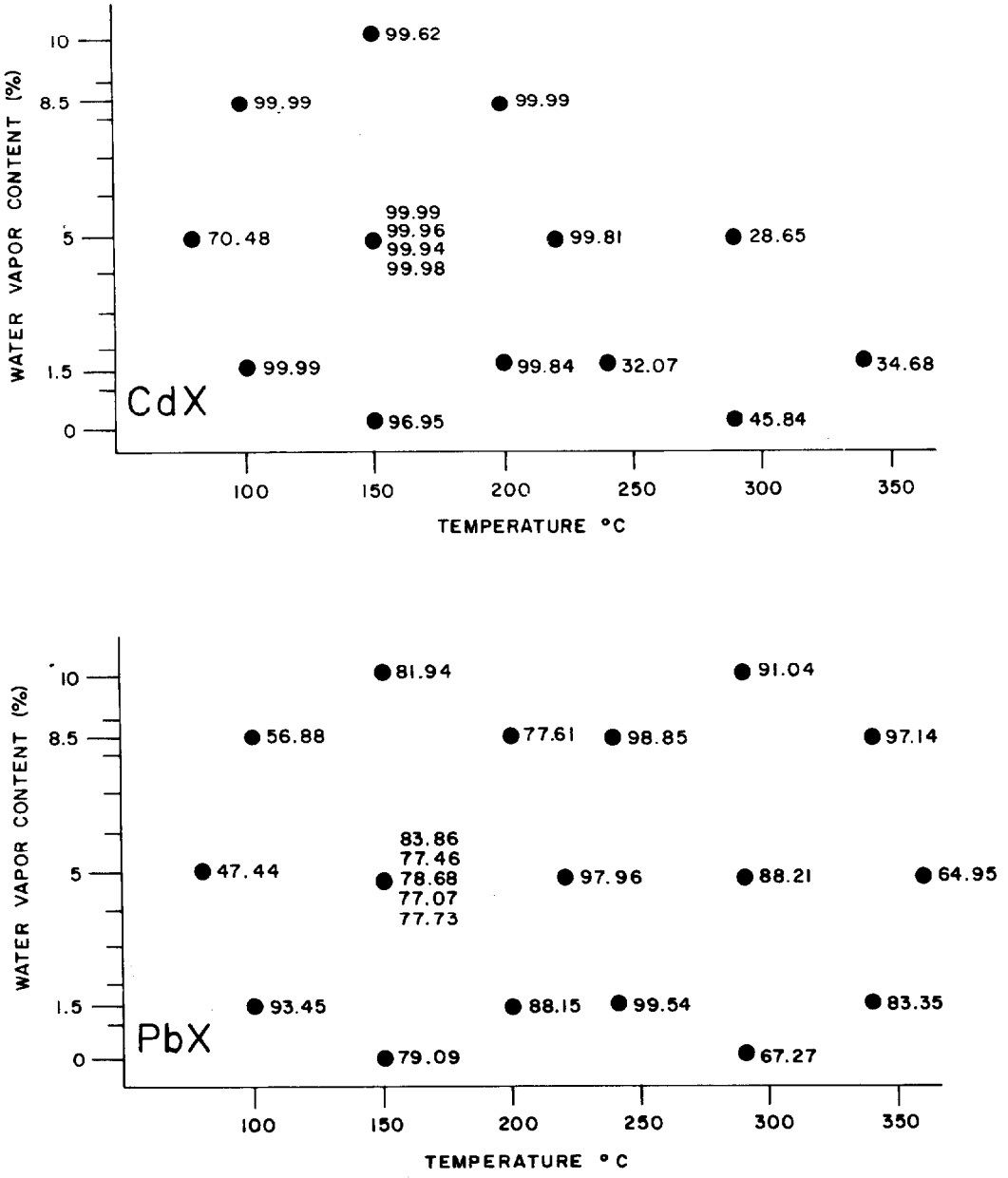


Figure 3. Screening Tests for PbX and CdX

Saturation Tests

Tests were conducted to determine the maximum-loading capacity of NaX, PbX, CdX and AgX under nearly static conditions. The adsorbents were saturated by exposure to airborne I_2 using a face velocity of 1 cm/sec and a bed temperature of 150°C until constant weight was obtained. They were then purged with air (up to 120 hr at 150°C) until the rate of I_2 desorption was negligible. The remaining iodine was considered chemisorbed. The results are given in Table III.

Table III

MAXIMUM IODINE ADSORPTION CAPACITIES OF METAL ZEOLITES AT 150°C. (mg I_2/g bed)[a]

Adsorbent	Saturated	Physisorbed[b]	Chemisorbed
NaX	364	334	30
AgX	349	135	214
PbX	179	153	26
CdX	374	329	45

(a) Based on dry weights of 0.61 g/cm^3 for NaX, 0.71 g/cm^3 for CdX and 0.85 g/cm^3 for PbX and AgX.

(b) Iodine removed from bed during air purge.

It was anticipated that all of the adsorbents would have saturation capacities similar to NaX. The lower capacity of PbX indicates that partial blocking of the adsorption sites is occurring. The chemisorption capacities of PbX, CdX and NaX are only about 9% of the saturated NaX capacity; no effect due to the cation is apparent. The data indicate that considerable chemisorption occurs in AgX.

Loading-Capacity and Effect Tests

The iodine-loading capacity of AgX at breakthrough (DF $\sim$ 200) was studied as a function of bed depth and face velocity. The data given in Figure 4 indicate:

(1) The loading capacities of the 10-cm beds are considerably larger than the 5-cm beds at all face velocities tested. No significant increase in loading capacity occurs between 10-and 15-cm-bed depths.

(2) A large decrease in loading capacity occurs with increasing face velocity at each bed depth.

(3) For bed depths 10 cm or greater, face velocities below 15 m/min would not greatly increase the loading capacity.

(4) The loading capacities of 5-cm-deep beds of CdX and PbX is less than 3.5 mg I_2/g bed (based on two sets of duplicate tests).

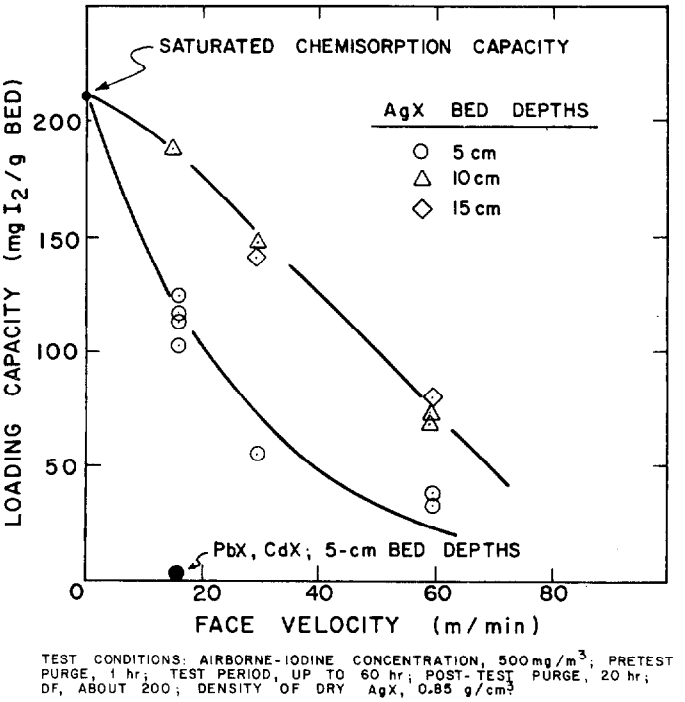


Figure 4. I_2 Loading Capacity of AgX in Dry Air at 150°C

Using a three-level-factorial design, the effects of bed temperature, water-vapor and NO_2 on the iodine-loading capacity of AgX were studied. The results are given below.

Table IV

EFFECT TESTS ON THE I_2-LOADING CAPACITY OF AgX

Bed Temp (°C)	Water Vapor (%)	NO_2 (%)	Loading[a,b] (mg I_2/g AgX)
100	0	0	139
200	0	0	94
100	5	0	67
200	5	0	35
100	0	2	32
200	0	2	37
100	5	2	42
200	5	2	55

(a) Loadings are based on a dry density of 0.85 g/cm^3

(b) Test conditions: bed depth, 10 cm; face velocity, 60 m/min; airborne-iodine concentration, 500 mg/m^3; pretest purge, 1 hr; test period, 5 to 16 hr; post-test purge, 20 hr; DF, about 200.

The data indicate:

(1) The main effect variables (temperature, water vapor and NO_2) cannot be analyzed independently because their interactions are so large.

(2) The interaction between water vapor and NO_2 decreases the loading from 67 to 42 mg at 100°C but increases the loading from 35 to 55 mg at 200°C.

(3) The interaction between bed temperature and NO_2 decreases the loading from 139 to 32 mg at 100°C and 94 to 37 mg at 200°C.

(4) Very little if any interaction between bed temperature and water vapor exists. The drop in loading capacity is about the same at both 100 and 200°C.

Iodine-Desorption and Recycle Tests

Iodine-desorption tests were run on AgX beds which had been loaded with iodine in dry-air streams at 15 m/min. The partial pressures of HI, which ranged between 0.0005 to 0.005 atmospheres, were obtained for several bed temperatures and superficial-face velocities throughout the test space. The rates of HI desorption were calculated by:

$$\frac{(P_{HI})(cm^3\ H_2/min)(128\ mg\ HI/24.1\ cm^3)}{(\text{cross-sectional area of the test bed})} = mg\ HI/min\text{-}cm^2$$

The response surface (see Figure 5) of the desorption rate vs the two experimental variables was obtained by fitting the experimental data to the second order model:

$$Y = 3.09 + 8.81X_1 + 2.93X_2 + 1.98X_1^2 + 0.26X_2^2 + 2.89X_1X_2$$

where the units for Y are mg HI/min-cm^2, X_1 = (temp-500)/100, and X_2 = (face velocity - 350)/250. All observed-desorption rates agree within 10.7 ± 5.8% (95% confidence level) of the predicted rates on the response surface. However a tailing effect at 400 and 500° occurs in which the P_{HI} continually decreases to zero after about 80 to 90% of the iodine is desorbed. The tailing effect causes the average desorption rate for 99%+ removal of iodine to be about 2.5 times less than that predicted by the response surface.

Recycle tests (see Figure 6) on three 5-cm-deep beds, in which iodine was repeatedly loaded and stripped, were run to test the effect of regeneration temperature on loading capacity. When regenerating at 600°C, the loading capacity decreased about three-fold after three cycles. Using regeneration temperatures of 400 or 500°C caused the loading capacity to decline about two-fold after five cycles. There is no apparent difference between using a regeneration temperature of 400 or 500°C, but a large one exists between 500 and 600°C. The total exposure of the beds to 400, 500 and 600°C were 500, 90 and 10 hr respectively.

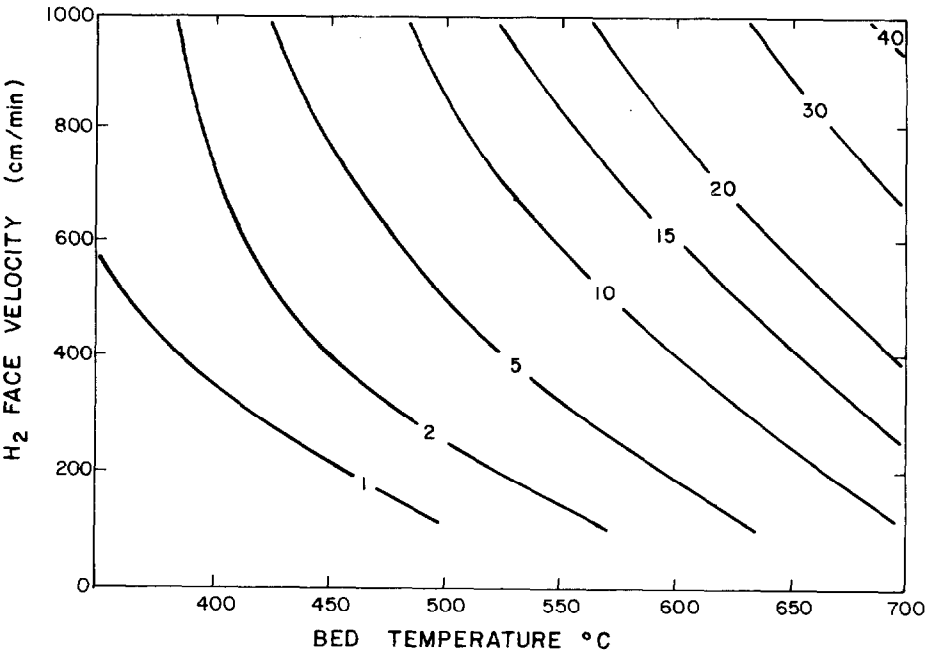
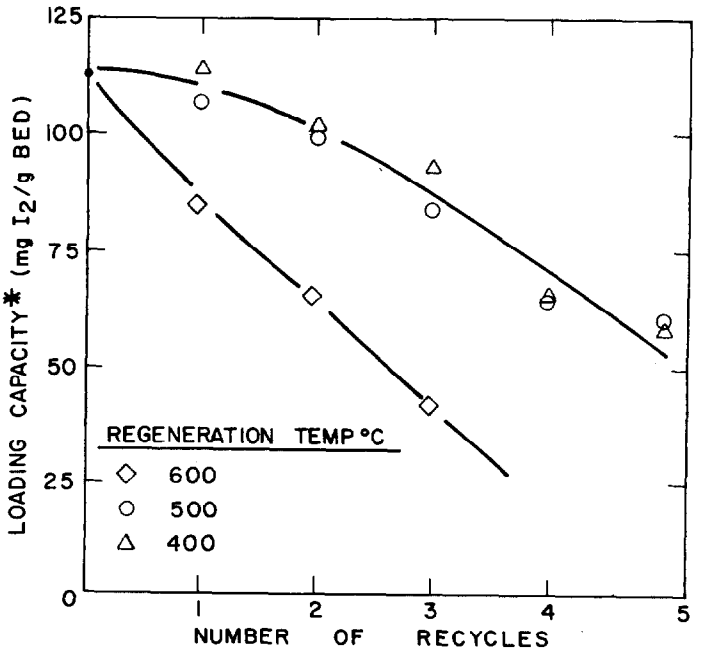


Figure 5. Desorption Rate of HI from AgIX(mg HI/min-cm^2)



* LOADING-TEST CONDITIONS: BED DEPTH, 5cm; FACE VELOCITY, 15 m/min; BED TEMPERATURE, 150°C; AIRBORNE-IODINE CONCENTRATION, 500mg/m^3; PRETEST PURGE, 1 hr; TEST PERIOD, UP TO 16 hr; DF, ABOUT 200.

Figure 6. I_2 Loading Capacity of Recycled AgX in Dry Air

The desorbed iodine was adsorbed on PbX beds at 150°C downstream of the AgX beds being stripped. Using a superficial-face velocity of 500 cm/min, an average loading capacity at breakthrough of 317 mg I_2/g PbX based on four tests was obtained. One of the loaded-PbX beds was post-purged with H_2 at 150°C for 16 hr and no detectible loss of iodine occurred. Another loaded-PbX bed was immersed in distilled water at room temperature for several days and the solubility of the adsorbed iodine was found to be about 26 mg I_2/100 mls H_2O.

DISCUSSION OF RESULTS

Chemisorption vs Physisorption

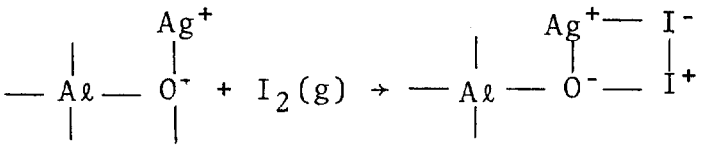
The tests on maximum-loading capacities (Table III) indicate that both physisorption and chemisorption occur in the substrate (NaX). The similar chemisorption capacities of CdX, PbX and NaX imply that the chemisorptive bonds which are formed are not metal iodide bonds per se, although bonding may be occurring near the metal sites. The chemisorption capacity of NaX at 150°C is about 30 mg I_2/g NaX. Therefore screening tests on metal-exchanged zeolites which are conducted at lower loadings can be misleading. Typically loadings of about 1 to 10 mg I_2/g substrate are used. Our screening tests (Table II and Figure 3) indicated that CdX might be an efficient adsorbent below 250°C. However, when the loadings were increased from 1.4 to 3.5 mg I_2/g CdX (Figure 4), the efficiency decreased. We decided that most of the data gathered for CdX and PbX represented the response of the substrate and had little to do with the exchanged cation.

The chemisorption capacity of AgX at 150°C is about 214 mg I_2/g AgX (Table III). This is 60% of the stoichiometric capacity based on the number of silver sites per gram. It can be inferred from the data in Table III and Figure 4 that there is a fundamental difference in the type of chemisorption which takes place in AgX as compared to PbX and CdX. If one assumes to the first approximation that the metal ions exist as oxides in the zeolite, the reaction taking place could be viewed as:

$$Ag_2O(s) + I_2(g) \rightarrow 2AgI(s) + \tfrac{1}{2}O_2(g)$$

$$MO(s) + I_2(g) \rightarrow MI_2(s) + \tfrac{1}{2}O_2(g)$$

where M = Pb or Cd. The standard free energies of the reactions are -16.1, 2.5 and 0.3 kcal/mole for Ag, Cd and Pb respectively. Similarly the conversion of Cu, Co, Fe, Ni, and Zn oxides to iodides involve positive-free energy changes of 20 kcal or more. All the above metal oxides are more stable than their corresponding iodides with the exception of silver, which may explain partially why only AgX has a large-chemisorption capacity. Since the oxygen anion is bonded into an aluminum tetrahedron, a plausible mechanism for the reaction taking place in AgX might be:



It would be expected that only partial bond breakage and formation would be involved to give a cyclic structure. But this reaction should also be thermodynamically favored because the iodide is more stable than the oxide and the O-I bond is stronger than the I-I bond.

Effect Tests

Application of adsorbent technology to reprocessing plants will generally involve bed depths greater than 10 cm. The results in Figure 4 point out the need to conduct tests with at least 10-cm-bed depths. Otherwise the predicted-loading capacities will be quite conservative. The data in Figure 4 also indicate a large loss in loading capacity with increased face velocity. However, it may be necessary to use high face velocities to avoid unfavorable ratios of bed diameter to bed length.

From the results given in Figure 4 and Table IV, one can infer that the conditions of optimum-loading capacity lie in the direction of lower temperatures, slower-face velocities and the absence of contaminant gases. This is of course to be expected, but practical application usually requires operating conditions which deviate far from ideality. Since the negative effects of increasing face velocity, bed temperature, NO_2 and water vapor are all large, the response surface of loading capacity as a function of all these variable will be studied. It is expected that face velocity will not interact with the other three variables.

Iodine-Desorption Thermodynamics

As previously explained, the formation of silver iodide (AgI) appears to be thermodynamically favorable in the reaction between I_2 and AgX. The rate at which HI is desorbed from iodine-loaded AgX (AgIX) also indicates that AgI is formed within the substrate. The reaction, which we believe occurs, is:

$$2AgI(s,1) + H_2(g) \rightleftarrows 2Ag(s) + 2HI(g) \qquad (1)$$

Assuming that the solid and liquid phases have unit activity in the substrate and the gases have unit fugacity, the free energy (ΔG) of reaction is given by:

$$\Delta G = \mu_{HI} - \mu_{AgI} \qquad (2)$$

Where μ equals the molar free energy of the compounds. The equilibrium partial pressure of HI (P_{HI}) is equated to ΔG by:

$$\log K_{eg} = \log(P^2_{HI}/P_{H2}) = -\Delta G/2.3RT \qquad (3)$$

where K_{eg} is the equilibrium constant. The experimental pressure of H_2 was maintained at one atmosphere. Therefore, equation (3) can be simplified to:

$$\log P_{HI} = -\Delta G^o/4.6RT \qquad (4)$$

where T = ^{o}K, R = 2 cal/mole, and ΔG is the standard free energy of reaction. Using values of μ^{o} for HI(g) from the JANAF tables[12] and values of μ^{o} for AgI(s,1) from the National Bureau of Standards,[13] the following data were calculated from equations (2) and (4):

$T^{o}C$	400	450	500	550	600	650	700
ΔG^{o}(kcal)	23.26	22.29	21.32	20.40	19.71	19.13	18.55
$P_{HI}(10^{3}atm)$	0.18	0.45	1.01	2.00	3.52	5.59	8.47

The calculated P_{HI} along with the observed P_{HI} (using a superficial-face velocity of 500 cm/min of H_2 through the test bed) are plotted in Figure 7. The observed P_{HI} is three times larger than the calculated P_{HI} at 400^{o}C. This corresponds to a standard free energy of formation of -12.76 kcal/mole for chemisorbed AgI as compared to -14.39 kcal/mole for the pure compound. Although the iodide bond is undoubtedly weaker due to a matrix effect, the discrepancy between partial pressures and free energies are small. At 600^{o} the discrepancy between partial pressures is less than 50%. It was also observed that at constant temperature, the P_{HI} was constant over a large range of H_2 flow rates which indicates that equilibration of equation (1) is instantaneous under these conditions.

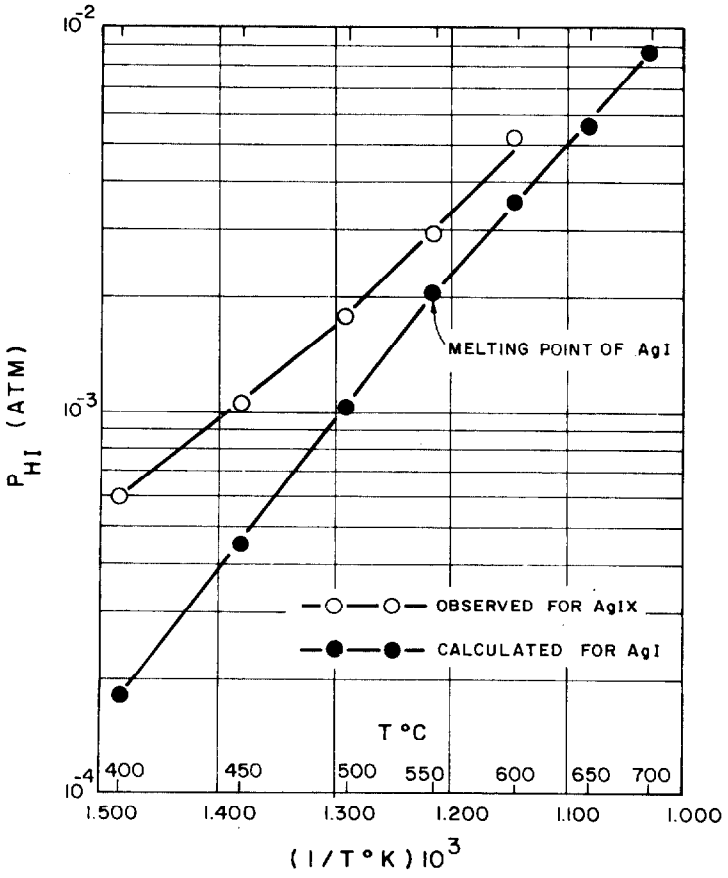


Figure 7. Partial Pressures of HI over AgI and AgIX

Recycle Tests

The loss in iodine-loading capacity of the recycled AgX (see Figure 6) is believed due to the progressive pore collapse of the zeolite structure. Studies by Thomas and coworkers[14] with Type 4A zeolite have shown that starting at 550°C a transformation of the zeolite phase into a non-zeolite solid occurs. The rate of the transformation increases with temperature and the resulting solid has virtually no adsorption capacity for water vapor. In our studies, silver whiskers were observed on the surface of the zeolite when the regeneration was performed at 600°C. It is possible that some of the AgI, which melts at 552°C, migrated to the surface and deposited silver after the iodine was desorbed. Considerable structural damage would be expected if this were occurring. At 500 and 400°C the silver deposit was not observed which may explain the large difference in the recycle data given in Figure 6 at 600°C vs the lower temperatures. We also observed that the rate of iodine removal from AgIX decreased to about half of its original rate by the fifth regeneration at both 400 and 500°C. This is again probably related to increased diffusion resistance from pore collapse. We plan to examine other silver-loaded substrates which have higher thermal stability.

Chemisorption in PbX

As previously mentioned the chemisorption of I_2 in PbX doesn't appear to be thermodynamically favored. However the reaction: $PbO + 2HI \rightarrow PbI_2 + H_2O$ has a negative free energy of -47 kcal/mole at 150°C. Since the oxygen anion is bonded into an aluminum tetrahedron, the reaction would involve the chemisorption of both iodine and hydrogen to form PbI_2 and two hydroxyl groups (i.e., 2 Aℓ-OH). In the absence of O_2 the chemisorbed PbI_2(PbI_2X) is stable at 150°C. Once cooled to room temperature, the PbI_2X is kinetically stable in the presence of air. A loading of 317 mg I_2/g PbX represents 88% of the stoichiometric capacity of the PbX based on the number of lead sites per gram.

APPLICATION OF ADSORBENT TECHNOLOGY

A typical application in a 5 tonne/day reprocessing plant might be to remove 600 kg/yr (iodine-129 plus iodine-127) of iodine from a 140 m^3/min off-gas stream. Assume that a loading of 50 mg I_2/g AgX could be obtained at a DF of 10^3 using a superficial-face velocity of 60 m/min in the presence of NO_2 and water vapor. Figure 8 illustrates a conceptual design of an iodine removal system which uses two-2 m^3 beds of AgX. The resulting bed dimensions would be a diameter(d) of 1.71 m and length (ℓ) of 0.86 m for a d/ℓ ratio of 2 and bed weights of 1.78 metric ton each. If the iodine-loading rate averaged 2 kg/day, then one of the beds would last about 40 days before breakthrough. Using a regeneration temperature of 500°C and a hydrogen-face velocity of 200 cm/min (flow = 4.66 m^3/min), the predicted desorption rate (from Figure 5) would be 1.5 mg HI/min-cm^2. When adjusted for tailing the average desorption rate would be about 0.6 mg HI/min-cm^2, which would require about 4.2 days to regenerate the bed. Each bed would be recycled about four times per year or 20 to 30 times in a five year period. During

this period the loading capacity would be declining and the frequency of recycle increasing. The important feature is that the loaded beds could easily be stripped of iodine and reused several times. This would permit small AgX inventories and more favorable d/ℓ ratios since a maximum loading would not be necessary. In the end, the silver could be reclaimed by conventional-wet-chemistry techniques provided the bed was not too contaminated by other radiosotopes. The stripped iodine would be loaded onto PbX beds for permanent fixation and storage. For 600 kg of I_2 about 2.5 metric ton or 1.7 m^3 of waste per year would be generated. The vessel would be designed so that it could both house the bed during loading and later be used for a storage container. Stoichiometrically, about 4.7 kg H_2 or 9 cylinders of H_2 would be needed per year.

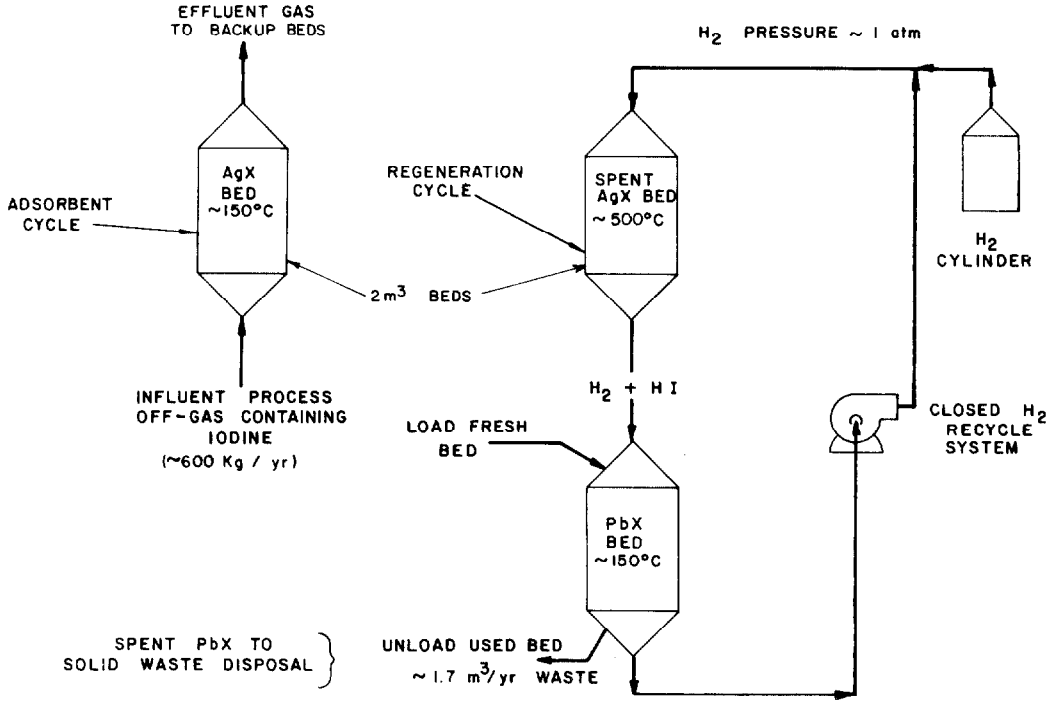


Figure 8. Adsorbent System for Iodine Removal
ACC-A-2180

If integrated-cleanup systems for the removal of HTO, NOx, iodine-129/131, Kr-85, etc. are required in the future, then it may be possible to simplify the regeneration process. In dry-nitrogen streams void of any contaminants, Collard and coworkers[8,15] have reported loadings up to 760 mg I_2/g substrate at 50% breakthrough using NaX at 25°C. Based on their mathematical analysis of the breakthrough data, it appears that iodine loadings in the range of 200 to 300 mg I_2/g NaX could be obtained with 10-cm-deep beds, face velocities of 15 to 50 m/min, and DF's of 1000. Since the reaction $I_2(\ell) + H_2(g) \rightarrow 2HI(g)$ has a negative free energy of -1.5 kcal/mole at 127°C, lower bed temperatures and faster regeneration rates would be possible than with AgX. The problem of pore collapse and loss of loading capacity should not be significant. The PbX would still

be used as the adsorbent for fixation and storage as the chemisorbed PbI_2.

APPENDIX A

Iodine-129 Abatement Potentially Required for LWR Reprocessing Plants

The following is assumed:

(A) The amount[1] of iodine-129 present in spent fuel is about 0.04 Ci per 40,000 MWD.

(B) The proposed EPA guideline[2] for iodine-129 release is a maximum of 0.005 Ci per gigawatt year electrical $(GW\text{-}YR)_{el}$.

(C) The conversion efficiency of thermal MWD to electrical is about 30%, therefore from assumption (A) there are 0.04 Ci iodine-129 per 12,000 $(MWD)_{el}$.

(D) Up to 90% of the iodine-129 is discharged as gaseous waste[1].

Based on these assumptions, the amount of unabated iodine-129 released would be:

$$(0.04\ Ci/12{,}000(MWD)_{el})(10^3\ MW/GW) = 0.0033\ Ci/(GWD)_{el}$$

$$(0.0033\ Ci/(GWD)_{el})(365\ day/yr)(0.9) = 1.095\ Ci/(GW\text{-}YR)_{el}$$

The required efficiency of an iodine-129 abatement system would be:

$$(1- (0.005\ Ci/1.095\ Ci))\ \ 100 = 99.5\%$$

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DISCUSSION

SKOLRUD: In your tests, have you evaluated loading of methyl iodides, or have you looked at the effects of organic contaminants?

STAPLES: The only contaminants we have looked at so far are NO_2 and water. We plan consideration of CH_3I and have discussed how to set up the experiments. We have to look at it because there are organic iodides in the off-gas stream. There have been past studies of the loading capacities of silver X for methly iodide. One number that comes to mind is about 200 milligrams of iodine per gram of silver X. Rather than repeat some of this work, we have gone to elemental iodine because that is probably the major iodine form released in fuel processing plants.

PARKER: Considering the intensity of capital costs of fuel reprocessing facilities, I wonder if you have done a complete economic study of this system.

STAPLES: We haven't done a complete cost analysis on this.

PARKER: Licensing is very difficult for reprocessing facilities. This hydrogen generation system could add more problems to licensing.

STAPLES: We believe that designing a fail-safe system to handle hydrogen is within our current technical capability.

DEITZ: We have estimated the thermal stability of potassium iodide relative to silver iodide by a thermal analysis procedure. When heated above 450°C the former appears to be more silver than silver iodide. The total iodine emission was determined and that from silver iodide exceeded that from potassium iodide. Is this your experience?

STAPLES: We have not made this comparison.

WILHELM: What is the price of silver zeolite, of lead zeolite, and of the regenration process, and is the decontamination factor of silver Z the same as for the X type?

STAPLES: Under the same loading test conditions, the DF's of silver Z and silver X appear to be the same. For Silver X, the latest cost figure I have heard was around $67 a pound if bought in ton lots. Lead X may cost about $12 a pound if bought in ton lots.

SKOLRUD: When regenerating loaded beds, is the HI sorbed on PbX stable? That is, is it chemisorbed or physically adsorbed?

STAPLES: We beleive the HI is chemisorbed by the PbX. We have performed purging and solubility tests which give us strong evidence to support chemisorption.

PARKER: What problems can arise in licensing fuel reprocessing plants with a H_2 regeneration system? For example, how much hydrogen does a plant producing 600 Kg of I_2 per year require?

THOMAS: Nine ordinary pressurized cylinders of hydrogen per year.

ORTH: Have there been tests in the H_2 regenerant diluted with some inert gas to reduce the hazard from an ignition standpoint? I worry about the safety analysis of a system with hot hydrogen gas containing the active iodine that we have gone to the pains of concentrating.

STAPLES: We have regenerated iodine-loaded silver zeolite only with pure hydrogen. Dilution of hydrogen with an inert gas would slow down the regeneration rate. For scale-up, we have discussed installing monitors to detect either leakage of air or outleakage of hydrogen. If either leak occurs, the process would be shut down and repaired.

Air Filtration Plants of Wall-Type for Separation of Fission Iodine in Nuclear Reactors

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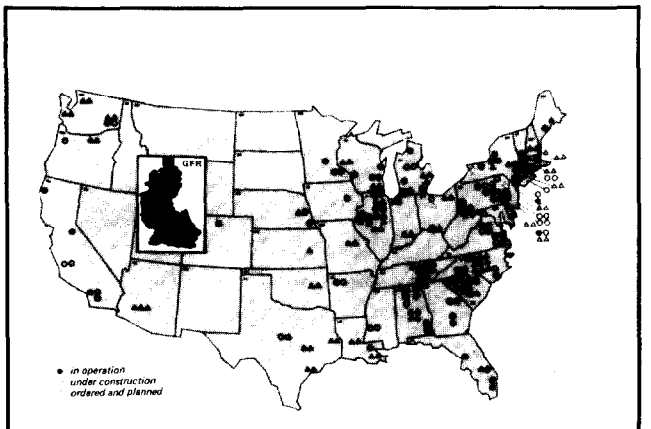
Abstract

The increasing density of nuclear power stations and increased safety requirements will lead in future to higher flow rates and longer residence times in the adsorption filter layer of the iodine sorption filter plants of nuclear power stations. The safety requirements in the Federal Republic of Germany have been complied with so far in the conventional way by means of duct-type filter constructions. For the higher flow rates and longer residence times necessary in future, we propose a filter construction of wall-type, which complies with the safety regulations of the Federal Republic of Germany. The economic and technical advantages are discussed.

The output of nuclear power plants has been standardized in the past years to values of 800 and 1200 MW and is expected to be maintained for the next 10 years. Contrary to this it is to be expected that the safety requirements will become more stringent during the next years on account of the increasing density of nuclear power stations and the increasing safety conscience of the public by taking advantage of the experience and new research results.



	USA		German F.R.	
	1975	1985	1975	1985
Inhabitants / km²	23	27	252	270
Nuclear Power Plants / km²	$6 \cdot 10^{-6}$	$24 \cdot 10^{-6}$	$36 \cdot 10^{-6}$	$144 \cdot 10^{-6}$

FIGURE 1:
Nuclear Power Plants USA and the Federal Republic of Germany up to 1985

Figure 1 shows a comparison between the density of nuclear power stations in the USA, and in the Federal Republic of Germany in 1985. Whereas in the Federal Republic of Germany an essentially higher density of nuclear power stations is planned than in the United States of America

on account of the greater population density related to the area of the country, there will be comparable nuclear power station densities in the densely populated area at the East Coast of the United States. The political consequences of this development resulted for example in the Federal Republic of Germany in passing the more strict regulation for protection against radiation (1). As examples are cited the increase of the all-year dosis ingestion factor for iodine to 4,4 x 10^5rem.m^3/Cisec, the consideration of the soil roughness when calculating the long-term dispersion factor and the necessity to consider of late the dosis values of all loading tracks at the thyroid gland dosis of 90 mrem. By maintaining strictly the principle "as low as practicable" a further reduction of iodine release has to be expected in the proceeding of approval for nuclear power plants. Therefore, it is necessary to discuss new ways for the concept of design of iodine sorption filters. Based on the safety layout criteria in the Federal Republic of Germany the present concept of construction of duct-type is presented and from this the proposed wall-type is being developed. Finally the technical and economical advantages of this type are being discussed.

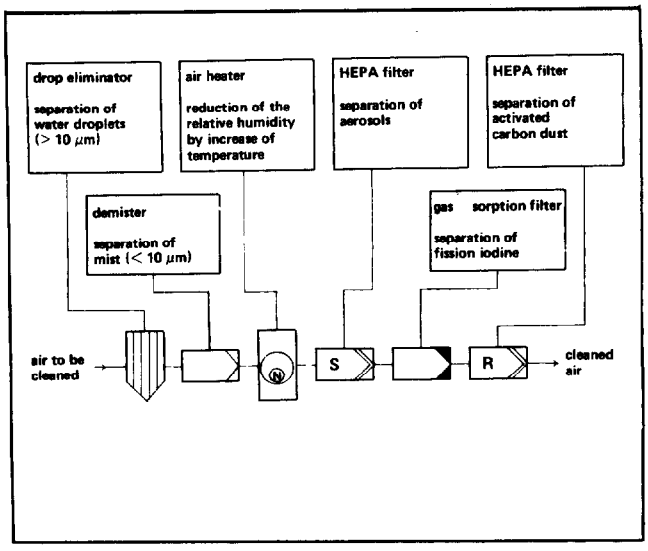


FIGURE 2:
HEPA filter and gas sorption filter plant for separation of aerosols and fission iodine

criteria	regulations
efficiency to DIN 24184	
1st filter stage	E ≥ 99,97 % } for paraffine oil mist
2nd filter stage	E ≥ 98 % } 0,3 < φ < 0,5 µm
leak-proof to DIN 24184	no oil mist thread visible by scattered light
tight filter seat	leak flow rate through filter seat < 0,01 % of the nominal flow rate
Prevention of activity release when changing filters	replacing of filter elements by means of protective bags

TABLE 1:
Safety concept for HEPA filter plant

Figure 2 explains the well known principal construction of iodine filters by means of the drop eliminator, the demister, which may at the same time serve as prefilter, the air heater for reducing the relative humidity, the HEPA filters for eliminiation of aerosols, the gas sorption filter for separation of fission iodine, and the HEPA filter for separation of activities attached to fines of activated carbon. According to the most important safety layout criteria given in Table 1 for the HEPA filter installations, the efficiency of the HEPA filter elements of the first filter stage must reach at least 99,97 % for a paraffin oil mist of 0,3 to 0,5 micrometer particle diameter. In the second filter stage an efficiency of 98 % is sufficient. In order to ensure that the efficiencies obtained in the type test are reached by the individual filter elements, these must be tested before installation for leak tightness by means of the oil mist test. During this test there shall be no visible oil mist threads in the scattered light of an intensive spot lamp. In order to guarantee the same efficiency of the individual filter elements also for the complete unit, the tightness of the filter seat that is between the gasket of the HEPA filter element and the sealing surface of the frame or housing must be suitable for being tested. For avoiding release of activity, replacing of the HEPA filter elements into a protective bag has to be made possible

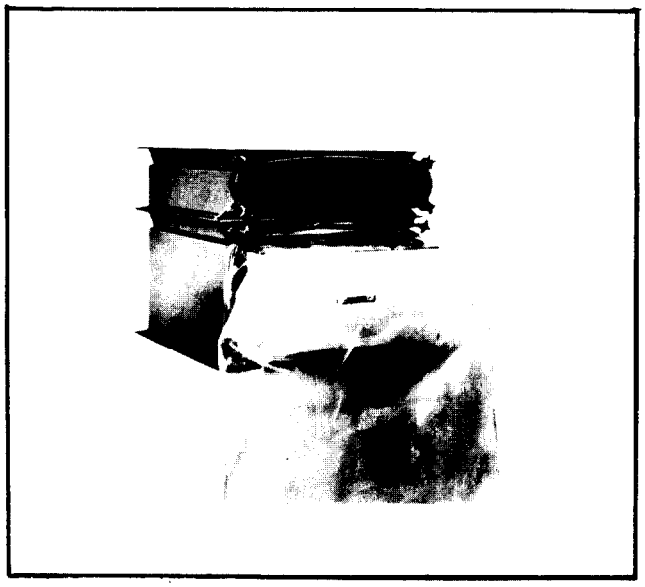


FIGURE 3:
Filter housing
consisting of prefilter for fine dust separation and HEPA filter with protective bag

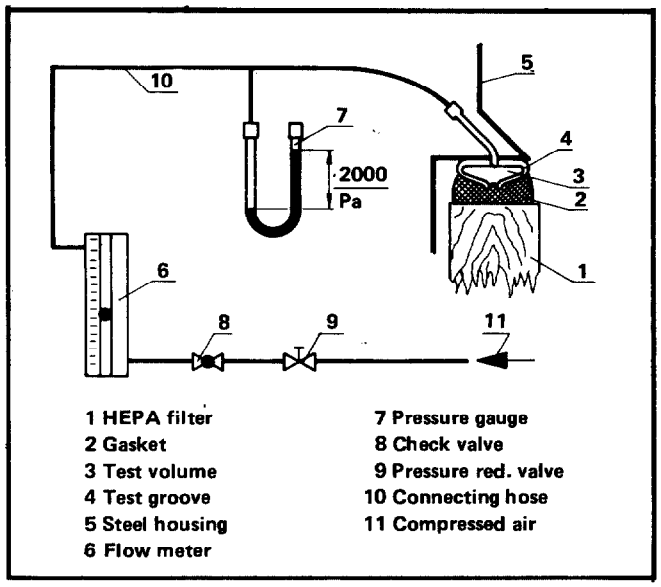


FIGURE 4:
Leakage test of filter seat for HEPA filter

as shown in Figure 3. – The principle of the filter seat test is explained in Figure 4. Air of a pressure of 2000 Pascal is pressed into a groove which is fitted gastight to the filter housing and is covered by the gasket of HEPA filter element. The leak flow rate given by the flowmeter shall not exceed 0,01 % of the nominal flow rate passing the HEPA filter element. Similar to the HEPA filter installations there are safety criteria for the iodine filters the most important of which are summarized in the Table 2. The efficiency for radioactive gaseous fission iodine in the form of methyliodine must be higher than 99 % for the off-gas filtration units, and higher than 95 % for the recirculated air filtration units.

criteria	regulations
efficiency for radioactive iodine	$E \geq 99$ % for CH_3 131 J for off gas $E \geq 95$ % for CH_3 131 J for rec. air
type	self-sealing fixed bed for accident filter
bed depth	minimum 200 mm for accident filter, addition with respect to the relative air humidity, loading with solvents and aging for reaching the required efficiency for 6 to 12 months.
checking of the sorption material during operation	By-passing of a partial flow rate through dismountable control filter
prevention of activity release when replacing the sorption material	replacing of the carbon by means of protective bags

TABLE 2:
Safety concept for fission iodine sorption filter plants

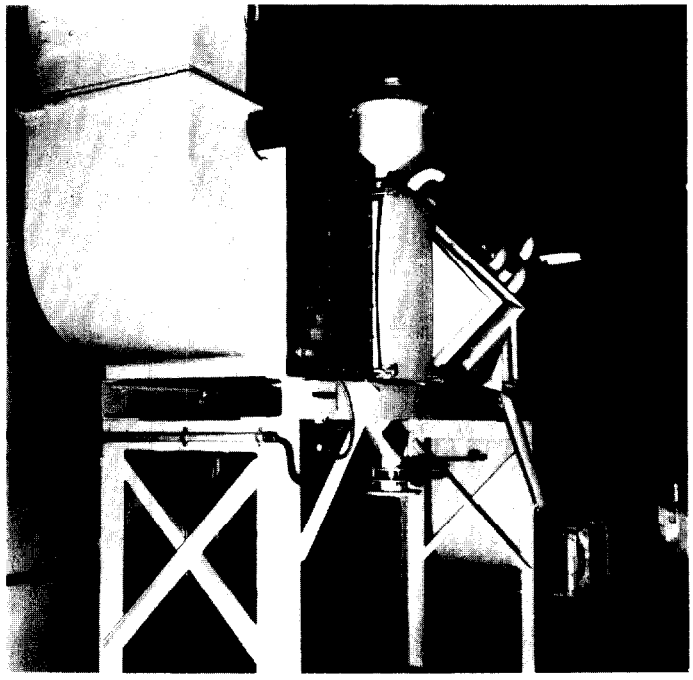
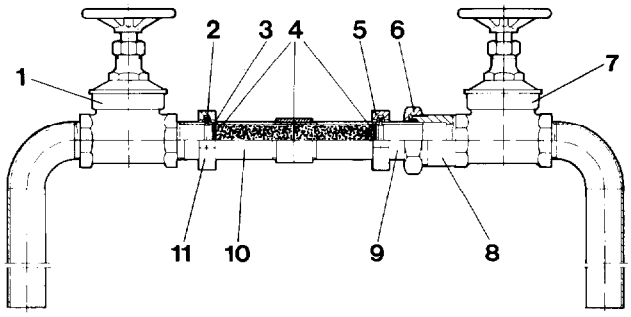


FIGURE 5:
Atmosphere cleanup system with fixed-bed iodine sorption filter, duct type

Accident filters must be of a self-sealing construction comprising a heaped fixed bed filter whose layer thickness must be at least 200 mm. When determining the layer thickness it should be ensured that the required efficiency is maintained for a period of 6 months to 1 year taking into consideration the relative humidity of the carrying air, the preloading especially by organic solvents and the aging of the sorption material. An example for the construction of such fixed bed sorption filters is shown in Figure 5. This filter may be charged and discharged with sorption material by airtight valves on top and at the bottom of the filter layer. For checking the sorption material during operation a partial airstream is separated and directed through removable control filters whose connections as shown in Figure 5 are parallel to the filter layer. Figure 6 shows such control filter. After dismounting the control filter the connections are closed by means of airtight valves.



1 Shut-off valve
2 Gasket
3 Gasket ring DIN 472
4 Stainless steel mesh
5 Clamp strap
6 Screw cap
7 Shut-off valve
8 Stuffing box stud
9 Pipe
10 Test adsorber
11 Clamp strap

FIGURE 6:
Control filter in parallel with sorption filter

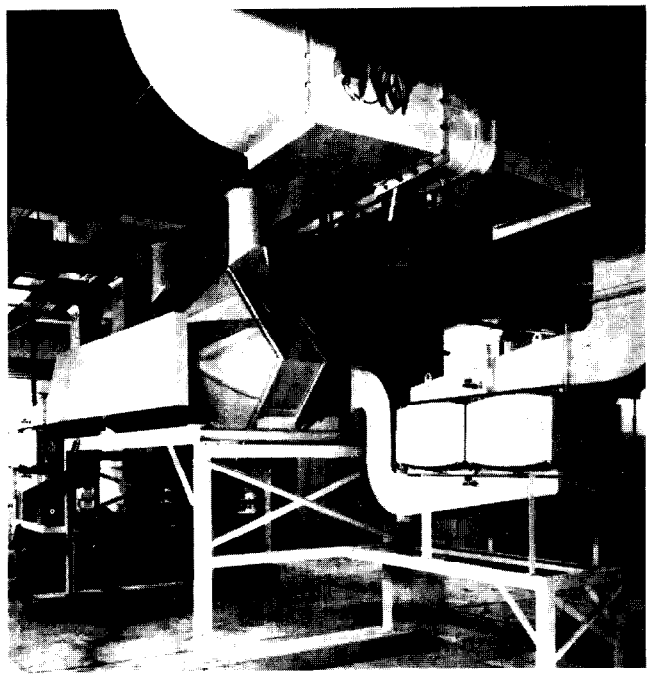


FIGURE 7:
Post accident off-gas filter plant, nominal flow 4000 m^3/h, in a nuclear power plant

The used sorption material of an iodine sorption filter bed is discharged into standardized waste containers. During this operation protective bags have to be applied for avoiding release of activity. According to the German regulations the iodine sorption filter units for filtration of waste air from controlled areas must be installed within the control range of the reactor. The technical realization of an accident off-gas filter plant for 4000 m^3/h such as installed in the Biblis nuclear power station is shown in Figure 7.

Equipments visible are the drop eliminator, the air heater, the first HEPA filter stage, the fixed bed sorption filter and the second HEPA filter stage. The fixed bed filters are installed at a height which allows discharge into standardized waste containers. Compared with this accident filter unit for 4000 m^3/h planned in 1972, the accident filters being planned today are provided for a flow rate of approx. 20 000 m^3/h. When maintaining the shown concept of filtration plant of duct-type for flow rates increased to 20 000 m^3/h, the following disadvantages will occur (2):

- high space requirement
- high material cost, especially for the stainless steel construction
- high production cost by working steel sheet for housing, connections and ducts

- high cost for 4-fold corrosion-resistant finish suitable for decontamination when using ordinary sheet metal
- difficult and time wasting decontamination
- increased pressure drop of the filtration plant caused by pressure loss in ducts, deviations, cross section changes, and consequently increased operating cost
- high transport and assembly cost.

The disadvantages given may be avoided if the HEPA filter stage and the fixed bed sorption filter are realized in wall-type while the safety criteria valid at present in Germany are maintained. HEPA filter walls with test groove for checking filter seat tightness which are equipped with oval rubber seals for replacing the HEPA filter elements by plastic bags may be assembled from frames by bolting or welding as shown in Figure 8. As the HEPA filter elements are completely surrounded by the plastic bag when removing them from the receiving frames, walls of this type may be serviced from the clean air side (3). The left half of the Figure shows the test groove and the leak rate measuring instrument.

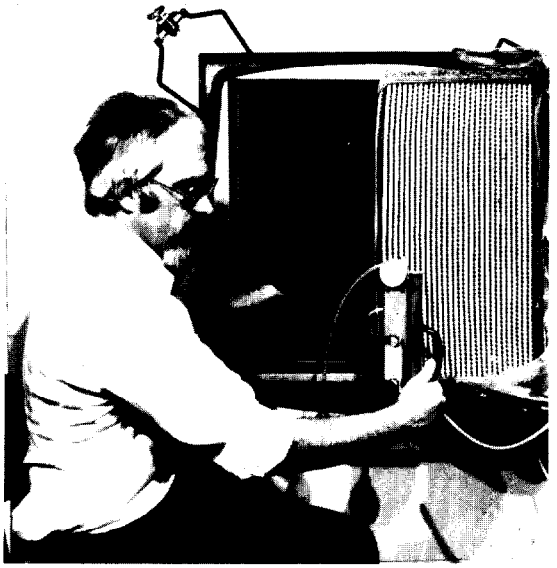


FIGURE 8:
Mounting frame for HEPA filter with filter seat test groove

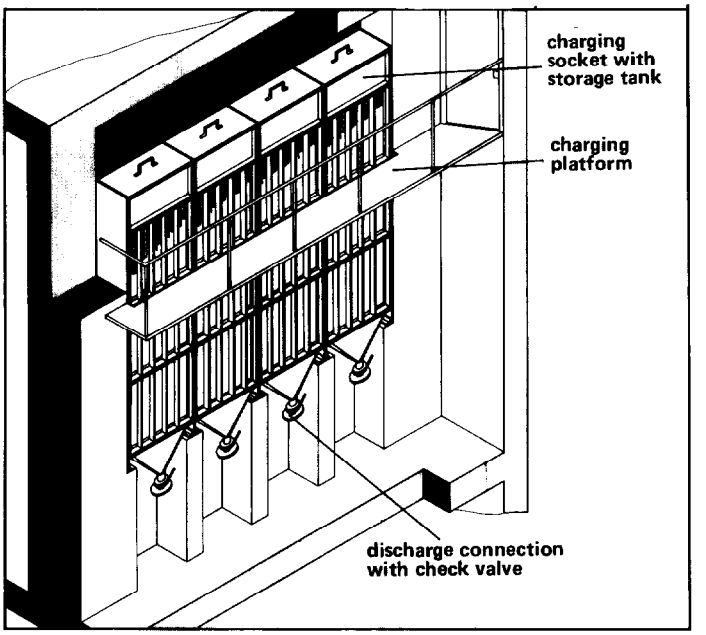


FIGURE 9:
Wall-type gas sorption filter for iodine separation

The view of the fixed bed sorption filter of wall-type seen from the clean airside is given by Figure 9. This shows 4 parallel filter sections, which may be filled after removing the cover from a maintenance platform on top of them. There is a spare quantity of sorption material arranged in the dead zone of the flow which settles automatically during operation in case of possible sagging of the sorption material, and which in this way prevents leakages between the inlet and outlet side of the filters. The used sorption material is discharged by means of a discharge connection into the waste container. The discharge connection is equipped with an sealing gasket in connection with plastic bags for replacing the sorbent. The control filter specified is arranged in such way that a tube is cast airtight in the concrete wall between the inlet and outlet side. This tube can be closed with an airtight valve on the outlet side of which the control filter may be vertically screwed. For reducing the danger of radiation for the maintenance staff the outlet connections may be discharged by means of tubes into the floor beneath. In addition it is possible to provide an automatic charging of the single filter sections from outside. When erecting the filter housing both of steel or of concrete paint finishing has to be provided in the clean room chambers which is suitable for decontamination. For protecting the sorption material from

preloading by organic compounds which are used in the nuclear power stations for example for repairs, painting and for decontamination, and which are of negative influence to the efficiency for methyl-iodine, among others there are at present considerations for using an adsorption prefilter (4, 5). This adsorption prefilter may also be realized as wall-type such as shown in Figure 9. It is arranged between the first HEPA filter stage and the gas sorption filter wall. This adsorption prefilter will increase the life time of the main sorption filter which has high safety significance and will ensure greater availability. The extra cost for the prefilter may be partially compensated by longer service life of the high-quality sorption material of the main filter and by the lower cost for safety control.

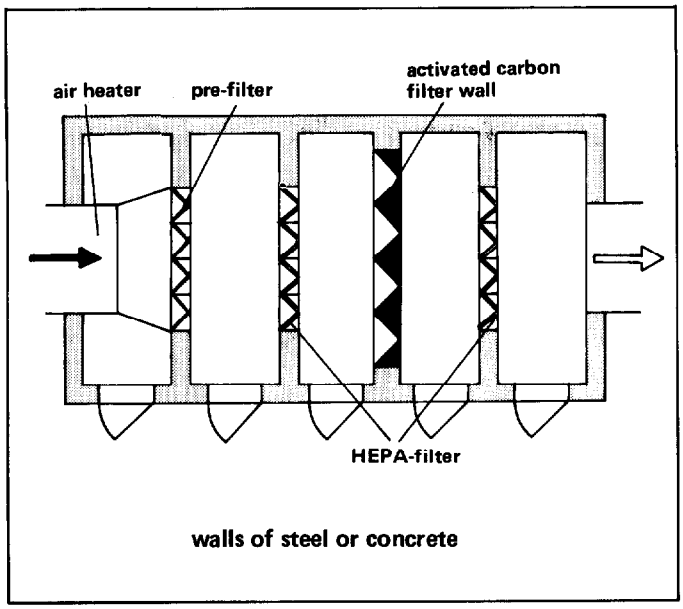


FIGURE 10:
Air filter plant of wall-type for 20 000 m^3/h, usual design

The new HEPA filter and gas sorption filter walls may be arranged in the classic parallel construction the way such as shown in Figure 10. The drop eliminator, demister and the air heater are arranged in the intake duct. In order to extend the service life of the first HEPA filter wall, a particulate prefilter wall is provided for. The flow velocity on the following HEPA filter wall is approx. 1,5 m/s at the nominal flow rate of the HEPA filter element. For avoiding high pressure drops and whirling up of the sorption material, the face velocity on the iodine filter unit has to be limited to 0,5 m/s. This change of cross section causes a non-uniform flow distribution over the face area of the sorption filter. This disadvantage is avoided by giving the same cross section to the HEPA filter wall and the activated carbon filter wall, which of course results in higher cost of the installation. Another possibility is arranging the HEPA filter wall and the sorption filter wall at angle to each other. This configuration is shown in Figure 11. It helps to reduce and uniform the air velocity before passing the gas sorption filter wall and to reduce the space requirement.

Comparison of cost was made for a four stage standard filter unit for 20 000 m^3/h of the conventional duct-type construction mentioned before, of the arrangement of parallel filter walls and of the arrangement of filter walls at angle to each other. This was based on an HEPA filter element being charged with an air flow rate of 1700 m^3/h and a residence time in the gas sorption filter of 0,6 seconds. The cost of the drop eliminator, the demister and the air heater were not included in the calculations as similar conditions were assumed in all three cases. For comparison all steel parts of ordinary steel were calculated with a 4-fold finish suitable for decontamination. Only the components of the gas sorption

filter wall were provided for of stainless steel. For all three cases it was assumed that a floor height of 6 meters is available. The prices for the walls of the plenum chambers of both wall types were calculated for construction of steel as well as of concrete. From the Figure 12 it can be seen that with the concept of filter walls arranged at angle to each other, 58 % of the space is required as compared with the concept of the duct-type air filter. A comparison of the respective prime cost of the filter walls arranged at angle to each other in a steel chamber and of the duct-type filter shows savings of 34 %. Another reduction in price is possible, if the filter walls can be mounted in a concrete room. In such case a saving of 44 % is possible. For the new plant design the values given for the reduction of space and prime cost are minimum savings.

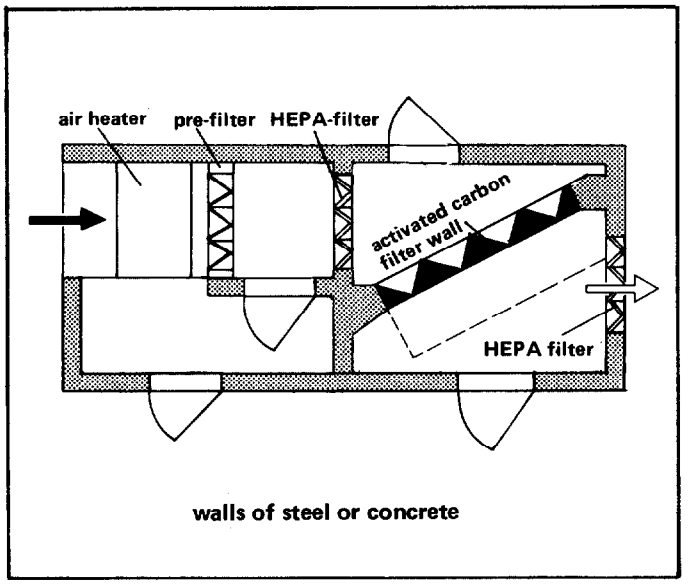


FIGURE 11:
Air filter plant of wall type for 20 000 m^3/h, compact unit

Type	steel housing	wall type	compact type
$\dot{V}$ [m^3/h] (cf/m)	20000 (11700)	20000 (11700)	20000 (11700)
Space required	100	70	58
Prime cost [%] steel walls	100*	73	66
Prime cost [%] concrete walls	–	62	56

Remarks: Prime cost for steel housing without wall equal 100 %

FIGURE 12:
Comparative cost analysis and space requirements for different types of filter units

Conclusion

Replacing of the conventional duct-type iodine filter units by wall-type filter designs while maintaining the safety requirements in Germany is technically feasible. A new HEPA filter wall with device for testing the tightness of filter seats and system of replacing of filter elements by plastic bag as well as a iodine sorption filter wall with heaped fixed bed are introduced. For filter plants of high flow rate and long residence time in the layer of the adsorbent the new solution will give an essential reduction of the space requirement and the production cost.

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(2) D. Sinhuber, M. Neumann, H.-H. Stiehl „Gassorptions-Filterwand zur Spaltjodabscheidung aus der Abluft von Kernkraftwerken", Doc. Nuclex 75, Coll. D 2

(3) C.A. Burchsted, A.B. Fuller "Design, Construction, and Testing of High-Efficiency Air Filtration Systems for Nuclear Application", ORNL-NSIC-65, January 1970

(4) J.G. Wilhelm „Verhalten von Jod-Sorptionsmaterialien", Euratom-Seminar, Dec. 1973, Doc. V/559/74

(5) J.G. Wilhelm etal., Jahresbericht 1973 der Gesellschaft für Kernforschung, KFK 1973

DISCUSSION

RIVERS: It's not unusual for nuclear reactor plant equipment to go to the low bidder. The lowest figure on your chart was for concrete structures. Our experience with concrete-cased units has been terrible, and I wonder how you cope with edge leakage and through-the-wall leakage?

STIEHL: As far as we've discussed this problem with the companies who make the concrete for the reactor buildings, they didn't see any problems. The sealing between the sorption filter stages and the concrete wall will be performed by the activated charcoal bed itself. To ensure the tightness of the HEPA-filter stages, experience with the installation of HEPA-filter walls for clean rooms are available. From the experience of running reactors, the diffusion of radioactive components through concrete walls can be avoided by careful concrete buildup and a special concrete coating on the walls. Nevertheless, steel construction will give fewer problems if uncontrolled leakage occurs during filter installation and repairs become necessary.

AN AIRBORNE RADIOIODINE SPECIES SAMPLER AND IT'S APPLICATION FOR MEASURING REMOVAL EFFICIENCIES OF LARGE CHARCOAL ADSORBERS FOR VENTILATION EXHAUST AIR

W. A. Emel*, D. Hetzer, C.A. Pelletier, E.D. Barefoot

and J.E. Cline

A. AN AIRBORNE RADIOIODINE SPECIES SAMPLER FOR NUCLEAR POWER PLANTS**

Abstract

A program, sponsored by the Electric Power Research Institute, is underway to determine the chemical species of radioiodine coming from LWR power plants and their persistence in the nearby environment. In support of this program,an airborne radioiodine sampler, developed and used by the AEC was modified and tested. This sampler consists of five components. The components are: 1) a particulate filter, 2) CdI_2 on a matrix of chromosorb-P to retain I_2, 3) 4-Iodophenol on a matrix of activated alumina to retain HOI, 4) silver exchanged molecular sieve-13X to retain organic iodides, and 5) impregnated charcoal to serve as a control. The AEC sampler has not been proof-tested for periods over 48 hours or for flow rates above 0.10ℓ/s For maximum sensitivity, a sampler is required to be used for periods of one to two weeks and at a flow rate giving a bed residence time of 0.1 sec. The AEC sampler was scaled up in size to attain an air sampling rate of 0.9 ℓ/s. Each media for this sampler (except the particulate filter) was tested in the laboratory for retention of the iodine species; I_2, Organic, and HOI. The tests were conducted at typical conditions observed at the main iodine release points at nuclear power plants. Confirmatory tests were run at operating nuclear power plants. The test results showed that under normal plant conditions the sampler could be operated at flow rates up to 0.80 ℓ/s and differentiate the iodine species I_2, HOI, and CH_3I. The retention efficiencies of each media for its specie of radio-iodine were found to be:

I_2 on CdI_2 - 87±5%, HOI on IPH 94±4%, and CH_3I on Ag 13-X or KI charcoal 99±1%.

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** Work performed under contract with the Atomic Industrial Forum.

I. Introduction

Extensive work was done in preparing activated charcoal air filters for nuclear power stations, to prevent a large accidental radioiodine release as had occurred at Windscale in 1957. Regular activated charcoal was found to retain essentially all of the elemental iodine, yet was rather inefficient to organic iodide, especially at high humidities. An extensive series of experiments by Collins, Taylor and Taylor at Windscale in 1967[1], showed that impregnated charcoals would solve the organic iodide problem. Maeck, Pence, and Keller developed a silver loaded zeolite with similar performance for retaining methyl iodide, but with some advantages over impregnated charcoal[2]. Cartan suggested the existence of a third chemical for of radioiodine[3]. At this time, the need for complete iodine species differentiating became apparent.

The Iodine Species Sampler was developed for air sampling for the proposed Loss-of-Fluid Test. The objective was to have a sampler which could differentiate non-iodine particulates, elemental iodine and organic iodine in steam-air mixtures.

The sampler which was tested is basically one which was developed and used by the AEC[4]. The sampler consists of five components. The components are: 1) A particulate filter, 2) CdI_2 on a matrix of chromosorb-P support to retain I_2, 3) Iodophenol on activated alumina to retain HOI, 4) Silver exchanged molecular sieve - 13X to retain CH_3I, and 5) charcoal to serve as a control. This sampler as it exists had not been tested for sampling periods over 48 hours or for flow rates above 0.11 ℓ/s. For the required sensitivity, the sampler is required to be used for periods of one to two weeks. It is desirable to operate the sampler at residence times >0.1 sec.

To increase the sensitivity, we scaled the AEC sampler to a 6.3-cm diameter size and retained the 2.5-cm depth. This larger sampler operates at flow rates up to 0.9 ℓ/s.

Each medium for this larger sampler was tested in the laboratory for retention of the iodine species; elemental, organic and HOI and for its limitations. Tests were conducted at typical conditions observed at the main iodine release points at nuclear power plants. These locations vary in temperature and humidity. The range of temperature is about 60°F for the lowest and 140°F for the highest. The range of humidity found at the major ventilation points is from 7% R.H. to 90% R.H. Confirmatory tests of the species sampler were run at operating nuclear power plants.

II. Previous Testing of the AEC Radioiodine Species Sampler

The first report on the performance of the radioiodine species sampler was given in the 11th USAEC Air Cleaning Conference[6]. In these tests, the sampler was run at 100 per cent relative humidity and at temperatures from ambient to 90°C. Due to the difficulty of generating pure HOI, the HOI test beds were preceded by a bed of CdI_2-chromosorb-P to remove the elemental iodine present. The results showed retention efficiencies of 99+% for elemental iodine on the CdI_2, IPH and CuX, retention efficiencies of 3-4% for HOI on CdI_2, and >95% for HOI on IPH and CuX, and retention efficiencies for organic iodide of <1% on all three media.

The copper zeolite beds exhibited breakthrough at high humidity when the beds were saturated with steam. Due to the difficulty of preparing Cu-Zeolite, it was abandoned as an HOI adsorbent in favor of 4-Iodophenol on alumina.

Additional testing of the AEC sampler was reported by Keller, et al at the 12th AEC Air Cleaning Conference[5]. Several tests were run to determine the samplers ability to differentiate iodine species at <100% R.H. In these tests, he found that the ability to differentiate species was good. Retention efficiencies for organic iodine were >99%, for HOI >80%, and for elemental iodine >90%. Again it was noted that there was little if any retention (<3%) of methyl iodide on the CDI and IPH adsorbents.

Kabat has tested two of the components (IPH & AGX) of the sampler for HOI retention[7]. The tests were at "room humidity"(55±5% relative humidity), iodine loadings of $\sim 10^{-3}$ $\mu g/m^3$, a residence time of 0.14 sec for a 30mm bed, and at ambient temperatures. His results indicate that the 5 weight % 4-Iodophenol-Alumina (30-60 mesh) supplied by Keller exhibited 20-40% breakthrough. The AGX tests showed a ~2% breakthough of HOI at 50% relative humidity and room temperature and a 30% breakthrough of HOI at 100% R.H. The results do not seem to be consistent with other reported data[8].

The sampler has been used to measure the iodine species in the delay line of a BWR[5]. It has also been used to measure iodine species for the USAEC Regulatory Operations program of independent measurements of radioactivity in BWR ventilation effluents[9] and by Reid in his work on removal of iodine by hydrazine sprays in containment[10]. The nuclear power divisions of both Westinghouse and General Electric have used the iodine species sampler. Performance data for the sampler, however is somewhat limited. The sampler was tested for use in experiments related to post accident radioiodine air concentrations. Post accident concentrations of radioiodine are significantly higher than the ventilation air concentrations found at nuclear power plants for which the sampler has been primarily used. The temperature and relative humidity conditions are also significantly different. Limited additional data has been presented [5,7] at conditions closer to plant air conditions. However, it is not complete and some information is contradictory. Further testing of this sampler under normal plant air conditions was required.

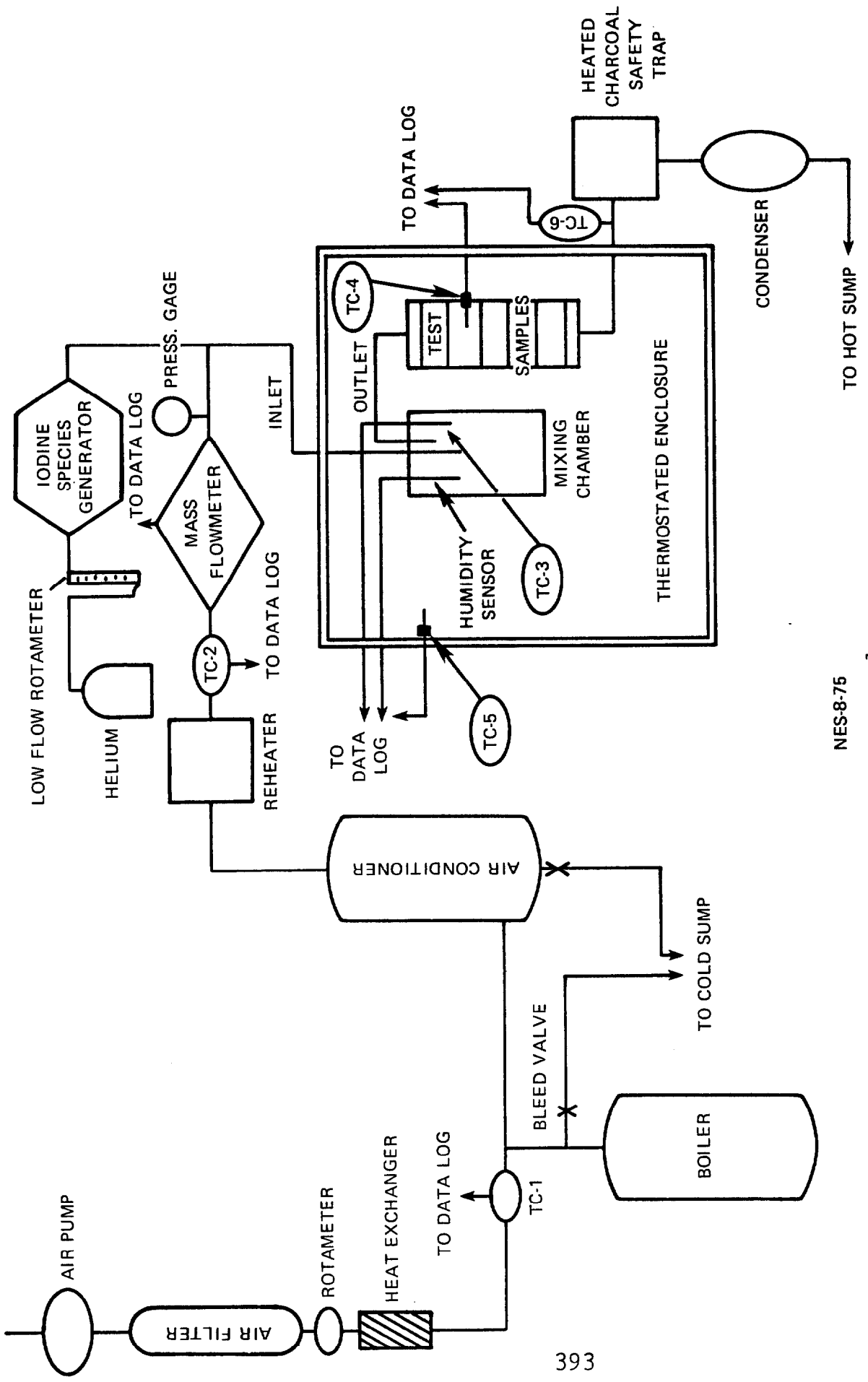
III. Test System for the Iodine Species Sampler

A. Equipment

The test system built for this study is similar to the systems used by Wilhelm[11], and by Pence[8]. The system is diagrammed in Figure 1. The inlet air is supplied by a carbon vane air pump. Pressurized supply air is filtered through a HEPA filter, two-2.5-cm beds of impregnated charcoal and another HEPA filter. The inlet air filters were installed based on recommendations in the RDT Standard M-16-1T[12]. The air then passes through an aluminum line which can be heated. After this point, water vapor, as required, is supplied by passing the air stream through a pyrex flask containing distilled water. The flask rests in a heating mantle. The air then passes through a pyrex "air conditioner" to adjust the temperature and relative humidity. The temperature of the "air conditioner" is controlled by a refrigerated circulator capable of output temperatures of -20° - +150°C, controlled to ±.05°C. Immediately downstream of the "air conditioner" is a second heater for reheating the air stream. Air then passes through a mass flowmeter where the flow is monitored. Downstream of the mass flowmeter is a pressure gauge. After the pressure gauge, an inlet is provided for the introduction of the different chemical forms of iodine. The iodine species are swept into the test system with a controlled helium purge of the iodine generator solution. Typical flows are 100-400cc He per minute . After the introduction of the iodine specie, the air passes directly into a thermostated enclosure to a stainless steel mixing chamber where the relative humidity and temperature of the air are monitored. The thermostated enclosure is an oven with mechanical air convection and a proportional heat controller. The oven has been modified for cooling by installing coils with circulating coolant. The air then passes through the test beds of media in the sampler. There is provision for monitoring the temperature in a maximum of two beds during a test. The air exits the oven, is reheated,passes through a heated charcoal safety trap, a water-cooled condenser, a vacuum pump and is exhausted to the hood.

The heating stations are individually controlled by variable powerstats. All parts of the air system downstream of the boiler are Type 316 stainless steel or pyrex. A minimum of 1.3cm of insulation is provided for the "air conditioner" and all tubing outside the oven. Data from the tests are logged on a 12-channel digital recorder. During a test, all data are logged at 5 minute intervals or on demand by the operator. The following data points are monitored: Temperatures: room air, inlet air, circulator supply to "air conditioner", downstream of reheater, circulator supply to oven, mixer, test bed #1, test bed #2, oven, backup bed reheater. Outputs from the mass flowmeter and the relative humidity sensor are also monitored.

Two rotameters were used in the system. 0-1.1ℓ/s capacity rotameter was used on the inlet air line and a second of 0-150 sccm air capacity was used to monitor and control the helium purge gas.



NES-8-75

FIGURE 1

A. Continued

The main flow monitoring device was a linear mass flowmeter with a range of 0-2.4ℓ/s air. The mass flowmeter was compared against a 0-4.7ℓ/s rotameter and 0-0.5ℓ/s mass flowmeter. In all cases, the output flows agreed within the error of the measurements. The specified accuracy of the mass flowmeter is ±1% of full scale for the output reading and ±2% of full scale for the meter reading with gas temperatures of 0° - 40°C.

Relative humidity measurements were taken with hygrosensors. The output signal of the sensor is converted and monitored. The output of the indicator was recorded by the data logger. Due to the importance of the relative humidity measurements, a check of the calibration of the two wide range sensors was made at the NES lab. The method used for checks was that first reported by Wexler and Hasegawa[13]. The sensors were reported to be accurate to ±1.5% RH. However, extensive recalibrations were required as the first checks indicated errors of ±10% RH at the higher humidities. The recalibrations were made using carefully thermostated salt solutions. The low range sensor has an operation range of 40°F and ∿5-45% relative humidity. This sensor was calibrated for three relative humidities at seven temperatures. The high sensor has an operating range of 40° to 140°F and ∿30% to 95% relative humidity. The high range sensor was calibrated for five relative humidities at seven temperatures. The accuracy is based on the error stated by Wexler of ±1% R.H. control of the saturated salt solutions and our measurement errors as determined by the deviation of the fitted curves from the measurement points. This latter error ranged from 0.07 to 4.1% relative humidity. Table 1 gives the estimates of error of the relative humidity measurements taken during the tests:

TABLE 1

Temperature	Measured % R.H.	Estimated Error
60°F	20%	±1% RH
60°F	90%	±2% RH
110°F	10%	±1% RH
110°F	83%	±4% RH

IV. General Description of Sampler

The in plant species sampler consists of five cups in series in an aluminum holder. The cups are machined from aluminum tubing and are 6.3 cm ID and 3.5 cm deep and have a 3-mm thick wall. An O-ring groove is machined at the inlet of each cup. The normal order of the cups as the sample gas sequentially passes through them is as follows: PF-particulate filter, CDI-cadmium iodide media for I_2 retention, IPH-4-iodophenol on alumina for HOI retention, AGX- or BC-151 charcoal-silver loaded zeolite or KI impregnated charcoal for organic iodine retention, and CH-BC-151 charcoal for a breakthrough monitor. The PF cup contains two F-700 filters, sealed by teflon washers and stainless steel snaprings. The filters are recessed 7mm

IV Continued

in the cup to allow for a plenum. The cups of media (IPH, CDI, and AGX) are loaded using paper filter on the front and a screen on the back to hold the material in place, retained by stainless steel snap rings. Each medium is loaded by weight and then packed lightly to give a 2.5-cm depth. To assemble the sampler, the cups, with o-rings are stacked in required sequence and placed in a 7.5 cm OD aluminum sleeve. The ends are attached by three long bolts passing outside the sleeve. The inlet and outlet on the sampler are stainless steel 0.95-cm tubing fittings.

V. Laboratory Tests

1.0 General Comments

1.1 Inlet Iodine Concentrations

Nominal total iodine concentrations in reactor building ventilation air have been estimated[1] at approximately 4 X 10^{-4} µgI/m^3. This value represents the fission produced iodine isotopes 127, 129, and 131. In addition, assumptions are made regarding decay and hold up time for fission product iodine in the fuel such that the weight ratio of Total Fission Product Iodine/^{131}I $\simeq$ 10 at the sampling point. Selection of the test iodine concentrations was made using the ratio of $\frac{\text{Total I}}{^{131}\text{I}} \simeq 10$, and the typical range of ^{131}I concentrations found at nuclear power plants. The typical range is 10^{-7} to 10^{-12}µCi ^{131}I/cc which translates into approximately 10^{-5} to 10^{-10}µg total I/m^3. Sufficient tracer was used to allow an accurate (±10% or better) measurement of a few per cent penetration of iodine specie through a test bed. In general, the test inlet concentration was ∿10^{-5} to 10^{-7}µg total I/m^3. The effect of ambient iodine (10^{-2}-10^{-3}µg total iodine/m^3) in plant exhaust is not considered. Any exchange of ambient iodine with the chemical species of iodine in the plant air would increase the individual species concentration. This would result in the same or higher specie retention by the specific media. The only ambient iodine in the tests is that which passed the two inches of charcoal adsorbent at the inlet to the test apparatus.

1.2 Iodine Tracer

^{131}I The tracer used for all the tests was high specific activity ^{131}I from Union Carbide in Tuxedo, New York. The iodine tracer contains typically 20-25 atom percent ^{131}I (Cat. #1-131-P-2). The inlet concentration was calculated using the total iodine collected on the sampler beds (correcting the specific activity for decay from the tracer calibration date to sample count time) and dividing this total iodine value by the total flow during the generation period.

1.3 Relative Humidity

The relative humidity was monitored at 5 minute intervals throughout each test. The stated % R.H. is a numerical average of the observed values during a test. Typical ranges of humidity were from 1% R.H. to 3% R.H.

1.4 Temperature

The temperature was also monitored at 5 minute intervals during a test. The typical range of temperature was 1°F.

1.5 Species Generation

As had been observed by other workers [5, 6, 7], pure species of HOI could not be generated at the low iodine concentrations used in these tests. The purity of HOI generated was ∿30 - 70% with the majority of the remaining species being organic iodide. A similar difficulty was experienced with the generation of elemental iodine. I_2 was generated with purities of ∿30% - 80% and organic iodides the bulk of the balance. A potential source of the problem was the small amount of epoxy resin used to seal the lid of the mixing chamber.

1.5 continued

There were no problems with the generation of methyl iodide. The CH_3I yields were high (20-80%) and the purity of the specie was greater than 99%. All species generation times were ∿1 hour followed by two hour purge at the test condition.

1.5.1 Methyl Iodide Generation

The procedure was based on the commonly used reaction: $(CH_3)_2SO_4 + 2NaI \xrightarrow[CaCO_3]{\Delta} 2CH_3I + Na_2SO_4$. Iodine tracer (0.1 or 0.5mℓ) in 0.05N NaOH was fed into ∿seven milliliters of water containing three milliliters of dimethyl sulfate and ∿100mg calcium carbonate. The solution was purged by helium passing through a bubbler tip at a flow of 200-400cc helium per minute. A hot air stream, from a heat gun, was intermittently directed at the flask base to keep the solution hot, but not boiling.

1.5.2 Elemental Iodine Generation

The chemical reaction used to generate I_2 was one which is commonly accepted. The reaction is as follows:

$IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$. Iodine tracer (0.1 or 0.5mℓ) was added to 1mℓ of 0.05N NaOH in a dropping funnel mounted on top of a reaction flask containing a 10mℓ solution of 50mg $NaIO_3$ in 2N H_2SO_4. The I_2 produced in the reaction was swept from the solution by a 200cc/min flow of helium into the test system.

1.5.3 Hypoiodous Acid Generation

The procedure for HOI was based upon passing I_2 through a solution with a pH of 12. The reaction is:

$$I_2 + H_2O \rightleftharpoons H^+ + I^- + HOI.$$

The I_2 generation method described in V.B.1.5.2 was used. The I_2 in the helium gas stream was passed through a glass frit diffuser in a gas washing tower containing ∿200 mℓ of 0.01N NaOH. The gas stream then passed into the test system.

1.6 Residence Times

The residence time calculations are based on the internal diameter of the test cartridge, the depth of the media, and the volumetric flow per unit time through the cartridge. The times are expressed in seconds as calculated from the expression

$$\frac{\text{Volume of Media}}{\text{Volumetric flow per second}} = \text{seconds R.T.}$$

1.7 ^{131}I Analysis System

All samples from the lab tests as well as the in-plant tests were counted on one of two gamma pulse height analysis systems. Both systems have computer controlled pulse height analyzers coupled with germanium gamma-ray detectors. The systems are calibrated using NBS standards. Each detector has a lucite structure for precise positioning of samples. Complete details of the systems, their calibrations, and procedures for use have been reported[14].

1.8 Efficiency Determinations

If a pure specie of radioiodine is generated, the efficiency of a media for that specie can easily be determined. The method is to measure the activity which penetrated the test media. This is accomplished by placing a total radioiodine adsorber behind test media. This was done in the methyl iodide tests on the AGX/CH media using impregnated charcoal as the total iodine adsorber. When a mixture of species are generated, as in the I_2 - CDI and HOI - IPH tests, this method cannot be used. An alternate method is the dual bed technique. This technique requires that of the species presented to the test bed, only one is retained with any significant efficiency. When this condition is met, two beds of the same media may be placed in series. The activity found on the second bed is a measure of the efficiency of the media for that specie.

In all tests, the assumption is made that the second bed has the same specie efficiency as the first bed. An extrapolation of the efficiency through successive theoretical beds was made for each test to calculate the total penetration of the first test bed. The following equation was used for all the tests to calculate the media efficiency:

$$\left(I - \frac{\mu Ci \text{ Bed B}}{\mu Ci \text{ Bed A}}\right) \times 100 = \% \text{ Efficiency.}$$

2.0 Organic Iodide Adsorber Tests

The tests for the retention of CH_3I on AGX in humid atmospheres and on CH (KI loaded charcoal) for dry atmospheres are presented in Table 2. A full species sampler consisting of a particulate filter, elemental iodine adsorbent, non-elemental inorganic iodine adsorbent, an organic iodide adsorbent, and a charcoal backup bed was used in these tests. The tests consisted of an approximate one hour generation of the methyl iodide followed by a two hour purge, all at the individual test conditions.

The tests show that less than 0.03% of CH_3I is retained on any of the media ahead of the organic iodide adsorber in the species sampler. The two tests with detectable radioiodine on the CDI beds had more elemental iodine generated than normal. The activity on these beds most likely is I_2 and not CH_3I. The lowest efficiencies were observed in tests with high humidities and AGX. The samples from the three tests where a few percent penetration occurred were rechecked. No explanation other than normal penetration could be found. The two high temperature - high humidity tests have results reversed from what one would expect. At the shorter residence time, the AGX has less penetration. The test with ($\sim$3% penetration) did experience a condition where the humidity sensor was pegged for $\sim$25 minutes. It is highly possible that condensation may have occurred in the bed. Excluding the one test, the efficiency of AGX for methyl iodide under these test conditions is 99-100%.

3.0 Elemental Iodine Tests

Test results for the retention of elemental radioiodine on CDI media are presented in Table 3. The sequence of the test beds was as follows: CDI bed "A", CDI bed "B", IPH, and CH.

Table 2

AGX/CH Media

Methyl Iodide Tests

TEMP. °F	% R.H.	RES. T. (sec)	INLET $\mu gI/m^3$	PER CENT RETENTION OF I-131 ON TEST MEDIA					
				PF	CDI	IPH	AGX or CH	CH	% Effi.
86	50	0.16	3.4(-5)	<.01	<.01	<.01	>99.99	<.01	>99.99
60	22	0.16	6.4(-6)	<.01	<.01	<.01	>99.99	<.01	>99.99
60	26	0.08	3.0(-6)	<.01	<.01	<.01	99.95	.05	99.95
60	90	0.16	2.2(-5)	<.01	<.01	<.01	99.94*	.06	99.94
60	90	0.08	9.1(-6)	<.01	<.01	<.01	98.79*	1.22	98.77
110	10	0.16	2.9(-5)	<.01	.02	<.01	99.98	<.01	>99.99
110	16	0.08	9.8(-6)	<.01	.02	<.01	99.98	<.01	>99.98
110	83	0.16	2.4(-5)	<.01	<.01	<.01	97.08*	2.92	96.99
110	81	0.08	1.9(-6)	<.02	<.02	<.02	99.22*	.78	99.21

* - AGX media

Table 3

CDI Test Data

Temp. ^{o}F	% R.H.	Res. Time (sec.)	Inlet $\mu gI/m^3$	% Efficiency
61	37	0.082	1.3(-6)	88.4
60	25	0.167	1.1(-5)	91.1
61	90	0.082	1.7(-6)	78.2
60	90	0.168	1.1(-8)	90.1
60	90	0.168	1.7(-5)	84.0
111	10	0.083	1.0(-6)	85.5
111	9	0.167	4.0(-6)	92.6
110	82	0.082	9.9(-7)	85.8
110	82	0.169	1.9(-6)	90.4

The CDI data has been corrected for HOI retention (3.9±1.4% of HOI in air stream). In all cases except one the correction resulted in an increase of <1% in the efficiency. The one case resulted in a correction of +3%.

The average efficiency is 87.3±4.5% within the range of conditions used for testing. There appears to be a correlation between residence time and the efficiency for radioiodine. At a flow rate of 0.9ℓ/s (0.08 sec. R.T.) the retention efficiencies are ∿84±4%. At 0.5ℓ/s the efficiencies are 90±3%. While these two groups of data are not mutually exclusive, there is a trend. It is logically consistent that for reaction times on the same order as the residence time the shorter the contact period for adsorption/reaction, the lower the retention.

4.0 Hypoiodous Acid Tests

The tests for the retention of HOI on the IPH media are presented in Table 4. The sequence of the test beds was as follows: CDI bed "A", CDI bed "B", IPH bed "A", IPH bed "B", CH. The two CDI beds were used to remove the elemental iodine present in the inlet stream.

4.0 continued

Table 4

IPH Test Data

Temp. °F	% R.H.	Res. Time (sec)	Inlet $\mu gI/m^3$	% Efficiency
60	21	0.092	5.8(-6)	98.9
60	20	0.155	1.3(-5)	94.1
60	90	0.080	8.2(-6)	80.5*
61	90	0.140	2.4(-5)	96.9
60	90	0.164	1.5(-5)	91.1*
110	11	0.117	1.8(-5)	93.4
109	10	0.155	1.0(-5)	95.6
111	50	0.111	9.4(-6)	98.3
110	83	0.081	9.2(-6)	30.1
109	82	0.052	4.1(-7)	78.3*
110	82	0.149	8.4(-6)	81.1*
112	78	0.147	5.3(-5)	99.2

*Tests run with bad batch of IPH

At the longer residence times of >0.1 sec, the efficiency of IPH for HOI is 94±4% using all data points. The test which gave 30.1% efficiency experienced condensation in the test beds. The relative humidity sensor was operating at its response limit and we exceeded not only 83% R.H. but 100% R.H. and condensation occurred. The bad batch of IPH was not detected until tests with high temperature and low humidity were run. Since previous tests had been run under the same conditions with radically better results (∿95% versus 37% efficiency), obviously something had failed. Several things were checked. When a new batch of IPH was prepared and tested the efficiencies did return to ∿95%. Upon further checking, it was learned that during the preparation of the suspect batch, a dark brown third phase formed when the 4-iodophenol was dissolved in the ligroin. A modification in the procedure remedied this problem.

4.1 Activity Profiles of Selected IPH Tests

In the last four IPH tests, the IPH test beds were removed in sections to determine their activity profiles. Each fraction of the first IPH bed contained within ∿10% the same amount of material and were well mixed before counting.

4.1 Continued

Test 39 - Conditions: 109°F, 10% R.H., 0.155 sec. R.T., Efficiency 95.5%, 1 inch deep bed

Section:	Front 1/4	Second 1/4	Third 1/4	Last 1/4
Per Cent Activity of Total Bed:	91.8±2.4	3.5±.6	2.7±.5	2.0±.5

Test 40 - Conditions: 60°F, 20% R.H., 0.155 sec R.T., Efficiency 94.0%, 1 inch deep bed

Section:	Front 1/2	Middle 1/4	Last 1/4
Per Cent Activity of Total Bed:	94.8±2.3	2.0±.3	3.2±.3

Test 41 - Conditions: 60°F, 21% R.H., 0.092 sec R.T., Efficiency 98.9%, 1 inch deep bed

Section:	Front 1/3	Middle 1/3	Last 1/3
Per Cent Activity of Total Bed:	92.3±1.3	6.5±.4	1.2±.2

Test 42 - Conditions: 110°F, 83% R.H. (Saturation occurred), 0.097 sec R.T., Efficiency 30.0%, Three IPH beds, each 1 inch deep.

Bed:	A		B		C	
Section:	First 1/2	Last 1/2	First 1/2	Last 1/2	First 1/2	Last 1/2
% Activity of A+B+C	32.0±1.2	18.9±.9	27.3±1.0	16.5±.8	2.2±.3	3.2±.3

The tests 39, 40, 41 show that more than 90% of the ^{131}I activity is on the front one-half inch of the IPH bed. Test 39 had ∿92% of the beds activity on the first 0.75 cm section.

Test 42 is presented to show the activity profile of a special sampler with three IPH beds in series which had been exposed to condensation. It is interesting that even under poor conditions, the retention of the HOI appears complete in three 2.5 cm thick beds.

4.2 Effect of 4-Iodophenol loading on IPH media

Before the tests were begun, it was suggested that five weight percent 4-iodophenol on alumina may work as well as ten weight percent. If this were true, the cost of the media would be reduced by 1/3. A series of tests were run to determine if any difference existed. In the tests, two identical samplers, with identical materials were run. One sampler contained beds of 5 w/o IPH media and the other had 10 w/o IPH media.

In two of the tests (60°F - 90% R.H., and 110°F, 50% R.H.), the two samplers were run at the same time, each using one half of the total flow. In these two tests, the residence time is calculated from the total flow and the proportion of the activity retained by each sampler. The results are presented in Table 5.

Table 5

Impregnant Effect on IPH Media

T °F	% R.H.	R.T. sec	Inlet $\mu gI/m^3$	% Eff.	Note
63	88	0.21	2.0(-5)	89.8	5 w/o MCB
61	90	0.140	2.4(-5)	96.9	10 w/o MCB
60	90	0.157	1.5(-5)	48.5	5 w/o MCB
60	90	0.164	1.5(-5)	91.1	10 w/o MCB
110	11	0.164	1.8(-5)	90.9	5 w/o MCB
110	11	0.117	2.3(-5)	93.4	10 w/o MCB
110	50	0.105	9.4(-6)	98.2	5 w/o MCB
110	50	0.111	9.4(-6)	98.3	10 w/o MCB
109	78	0.125	4.9(-5)	93.0	5 w/o MCB
110	78	0.147	5.3(-5)	99.2	10 w/o MCB

In every case the 5 w/o IPH had a lower efficiency. There is a significant difference in the efficiency 5 w/o IPH at the combination of lower temperature and high humidity, as indicated by the 48.5% efficiency at 60°F and 90% R.H. This value looks anomalous. Since both the 5 w/o and 10 w/o samples were run simultaneously under the same conditions, it is felt that the value of 48.5% maybe real. While it is possible to use 5 w/o near the high temperature range tested, the 10 w/o is recommended. Based on these results all further tests were made with 10 w/o IPH.

4.3 Effect of Mesh Size on IPH Media

A brief evaluation of the effect of the grain size of the IPH media was made at an operating nuclear power plant. Two samplers were connected to a stainless steel manifold to sample the same vent air. The inlet air concentration was $\sim 10^{-10}\mu Ci\ ^{131}I/cc$ or $\sim 10^{-8}\mu gI$ total/m^3. The samplers were run for 382 hours, sampling an air stream of 121°F and ~10% R.H. About 162 m^3 of air was sampled during the test. The results of the test are presented in Table 6.

Table 6

IPH Mesh Size Comparison

Cup	5 w/o IPH 20-40 mesh (Tyler) Percent of Total Sampler	5 w/o IPH 8-14 Mesh (Tyler) Percent of Total Sampler	Previous Measurement 5 w/o - 20-40 Mesh Percent of Total
PF	29.5	19.1	27
IPH-A	63.8	34.5	66 (47% I_2 + 19% HOI)
IPH-B	<2%	3.7	--
CH-A	6.7%	42.7	7
CH-B	<2%	<3%	<3%
Residence Time	∿0.11	∿0.19	0.12 est.

The 20-40 mesh IPH results agree well with a previous 170 hr species sampler that was taken in the same location. The data show a significant fraction of the I_2 and HOI breakthrough the large mesh IPH. They are collected on the first charcoal bed along with the organic iodide fraction. The results clearly show that 8-14 mesh IPH is inferior to 20-40 mesh IPH.

4.4 Change in IPH Efficiencies by Varying the Substrate

The procedures for preparing IPH media call for "activated alumina" as the base material for the 4-iodophenol. No type of alumina was specified. For the early tests in this study, activated alumina (Cat. #AG612-1) supplied by Matheson Coleman and Bell was used. After the AGX/CH tests, it was learned that MCB no longer supplied the AX612 alumina. An alternate source was found at Fisher Scientific. Their activated alumina, Cat. #A541, in 8-14 mesh, was ground and sieved to 20-40 mesh and used in the first IPH tests. The results of the tests are in Table 7.

Table 7

HOI Efficiencies of IPH Media Based on Fisher A541 Alumina

T °F	% R.H.	R.T. (sec)	Inlet $\mu gI/m^3$	% Efficiency
61°	47	0.158	1.6(-5)	93.7
63°	85	0.168	5.6(-6)	<10
111°	9	0.147	4.9(-6)	92.3
110°	82	0.145	2.6(-6)	38%

The high humidity data were surprising. All published information had indicated IPH had better performance at high humidities. The published data gave >80% efficiency at lower humidity. An immediate investigation was begun into the source of the problem. The only change that had been made in the IPH was the source of the alumina. It was learned that two distinctly different types of activated alum-

4.4 continued

ina were involved. The original MCB AX612 was cleaned and sieved from Alcoa type F-1 alumina, a crystalline, highly active material. The Fisher A541 was Alcoa type F-5 activated alumina. Type F-5 is made from type F-1 and has ∿12 w/o $CaCl_2$ added to it. A supply of Alcoa type F-1 28-48 mesh activated alumina was secured for use in completing this study. The alumina was sieved as is and the 30-40 mesh fraction used in preparing the IPH media.

4.5 Retention of I_2 on IPH

As could be predicted, elemental iodine is retained on IPH media. Two tests were conducted to verify this. The tests were made by reversing the order of media in one sampler (PF/IPH/CDI/AGX/CH) and comparing the results with a sampler using media in the normal sequence (PF/CDI/IPH/AGX/CH). The sum of the activity on the CDI and IPH beds in the normal sampler should equal the activity on the IPH beds in the second sampler. The data are presented in Table 8. The tests were run under the same conditions ∿110°F, ∿10% R.H. for the same period of time ∿22 hours. The results clearly show that IPH is a good adsorber for I_2.

Table 8

I_2 on IPH

Normal Sampler			Reversed Beds in Sampler	
Component	% Total ^{131}I		Component	% Total ^{131}I
PF + CDI	67.8	→91.0	PF + IPH	90.2
IPH	23.2		CDI	<1.5
AGX	8.9		AGX	8.7
CH	<1%		CH	<1%

4.6 IPH Reproducibility

A test was designed to determine the performance reproducibility of two different batches of IPH media, Batch #5 and Batch #8. Both batches were prepared using the same materials and the same procedure. The two batches of IPH were loaded into the aluminum cups and the cups loaded into the samplers in the following sequence: CDI/CDI/IPH-A/IPH-B/CH. They were run through the standard one-hour HOI generation and two hour purge. After the purge, the test beds were removed and counted. The IPH-A beds from the two samplers were then placed in new samplers for purging. The new samplers were loaded in this sequence: IPH-A/CDI-P/IPH-P/CH-P. The results are listed in Table 9 and Table 10.

Table 9

IPH Batch Comparison

Conditions: 110°F, 10% R.H., inlet concentration 4.6(-5)μgI/m^3, HOI Purity 72%.

	IPH Batch #5	IPH Batch #8
Residence Time:	0.12 sec	0.23 sec
HOI Retention:	98.2±.2%	99.2±.3%

4.6 continued

Table 10

Purge Tests of IPH Batch Comparison

Conditions: Lab air, 6 slm flow rate, 18.5 hr duration, 75°-80°F. 20-60% R.H.

Component	IPH Batch #5 Percent of Total	IPH Batch #8 Percent of Total
IPH-A	97.0±2.2	96.1±1.4
CDI-P	<0.2	<0.2
IPH-P	1.6±.2	1.9±.4
CH-P	1.4±.2	2.0±.5
Total Loss	∿3%	∿4%
Bed Sections		
First 1/3	99.0±3.0	97.5±1.8
Middle 1/3	0.8±.4	1.0±.3
Last 1/3	0.2±.1	1.5±1.4

The two batches compared quite well. The losses of ^{131}I during the purge, though small, again may be due to the heavy organic iodide from the mixer resin. Losses of ∿6% of the activity on the IPH bed were observed for purges of 4 days. It is possible that the losses are due to oxidation of the iodine bound to the 4-iodophenol near the surface of the alumina particle. If this is the case, the rate of loss would diminish as a function of time and would not exceed ∿6%.

VI. In Plant Tests

A series of tests were run to compare with laboratory data. Each media (CDI, IPH, AGX), were run for ∿two week periods at operating plants. Two studies were made of the species sampler's stability over 4 to 48 hours. A study of the form of iodine lost during 4 day lab air purges of samplers returned from the field. These studies are detailed below.

1.0 Special Dual Bed In-Plant Break-Through Tests

Special samples were run in 2-3 week tests at two of the plants. One method for verification of sampler media is the dual bed technique. This technique involves placing two cartridges of the same media in sequence in a sampler. It assumes that a chemical form of iodine is retained with the same efficiency by both beds. Therefore, the amount of radioiodine retained on the second bed is considered breakthrough. This method can easily be used with media that have retention efficiencies greater than 75%. We have used it for testing of the CdI_2 and the Iodophenol.

1.1 CDI

Three dual bed tests have been run to date. These are listed below. The results indicate a 10% to 20% loss of radioiodine when CdI_2 is run from 9 to 18 days.

CDI

Test	1	2	3
Run Time	210 hrs.	310 hrs.	432 hrs.
$\mu Ci\ ^{131}I/cc$	10^{-10}	10^{-12}	10^{-12}
Temperature	105°F	120°F	120°F
Rel. Humidity	<10%	<20%	<20%
Residence Time	0.13 sec.	0.1 sec.	0.12 sec.
Breakthrough	9.0%	16.6%	18.6%

1.2 IPH

Again, three dual bed tests were run. The results show essentially no breakthrough for two week exposures.

IPH

Test	1	2	3
Run Time	359 hrs.	358 hrs.	432 hrs.
$\mu Ci\ ^{131}I/cc$	5×10^{-9}	3×10^{-9}	2×10^{-10}
Temperature	105°F	120°F	120°F
Rel. Humidity	<10%	<20%	<20%
Residence Time	0.1 sec.	0.1 sec.	0.1 sec.
Breakthrough	0.3%	0.7%	<1%

2.0 Study of Sampler Stability Over 48-hour Periods

To study the ability of the sampler to differentiate species over 48-hour periods, two comparison studies were performed. In these measurements, parallel samples were collected simultaneously. One of these was collected continuously for 48 hours and the other was changed every 4 to 24 hours. Comparisons could then be made between the results from the shorter and the longer sampling periods. The results of these measurements are shown below. The uncertainties listed are the two sigma counting error.

2.1 Test #1 - 120°F, <20% Relative Humidity

(% ^{133}I Retained)

Duration of Sampling (Hours)

Media	4.4	15.8	24.1	44.3	Average of 1st 3
PF+CdI_2	68±7	78±8	83±8	74±7	76±6
IPH	27±3	19±4	12±3	22±4	19±3
AgX	4±1	4±1	5±1	4±1	4.3±1.0

2.2 Test #2 - 100°F, ≅40% Relative Humidity

(% ^{131}I Retained)

Duration of Sampling (Hours)

Media	13	11.3	13	13.3	51.2	Avg. of 1st 4
PF+CdI_2	66±6	63±6	63±6	69±7	60±6	65±6
IPH	27±3	29±3	28±3	23±3	31±3	27±3
AgX	8±1	8±1	9±1	8±1	9±1	8.3±1.0

The data indicate that under the conditions of these tests there is no evidence of any change in the performance of the species sampler during the span from 4 to 48 hours.

3.0 Loss of Iodine From Species Components During Purging

Tests were made to evaluate the losses from each component of the species sampler from a continuous flow of air through the media after the activity had been deposited. These measurements were made in such a way so as to determine also the species form of the activity being removed from each media. Samples collected in the plants were purged with air containing no radioiodine in two experiments. The first of these used normal air containing normal concentrations of stable iodine. The second used air filtered through charcoal used to remove the iodine from the air. In the experiments, the initial species sampler was disassembled and each component was used as the front section of a new species sampler. Following the purge, each component was analyzed for activity. The results are described as follows.

3.1 Test 1

Unfiltered Air

Length of Purge: 94 hours
Temperature: 73±2°F
Relative Humidity: 60±15%

		Original Cartridge		
	PF	CdI_2	IPH	AgX
% Loss from each Component	63.8%	5.4%	6.2%	3.2%
Form				
Particulate	5.9%	3.4%	<.1%	<0.3%
I_2	85.9%	73.8%	2.3%	<0.3%
HOI	6.1%	22.8%	54.6%	<0.3%
Organic	2.1%	<.1%	43.1%	>99%

PF

The results indicate a significant loss of iodine from the particulate filter. The chemical form was primarily elemental. The small (6%)amount of ^{131}I collected on the 2nd PF is possibly due to adsorption of I_2 as it passed through.

CdI_2

Approximately 5% of the ^{131}I retained on the CdI_2 was lost over the 4 day period. Once again a small fraction (∿4%) of the ^{131}I was retained on the PF. Again this is possibly due to elemental iodine adsorption. The loss from the CdI_2 was mostly elemental (75%) and the balance HOI.

IPH

The loss from the IPH cartridge was ∿6% of the total and was mostly HOI (55%) and Organic (43%). A small amount (∿2%) of elemental was observed.

AgX

Organic iodine was the only form lost that could be detected. The amount lost was ∿3%.

Filtered Air

Length of Purge: 94 hours
Temperature: 75±3°F
Relative Humidity: 70±20%

3.1 Continued

		Original Cartridge		
	PF	CdI_2	IPH	AgX
%Loss from each Component	7%	<1%	∿2%	∿3%
Form				
Particulate	38%	--	<0.4%	<1%
I_2	57%	--	<0.4%	<0.4%
HOI	<1%	--	<0.4%	<0.4%
Organic	5%	--	>99%	>99%

In contrast with the previous test, little radioiodine was removed from any of the species components. The particulate filter lost ∿3% of the second count. The loss was ∿1/3 "particulate" (probably elemental) and ∿2/3 elemental. No detectable (<1%) ^{131}I was lost from the CdI_2 cartridge. In the previous test, ∿5% of the ^{131}I was lost as I_2 and HOI. On the IPH Cartridge, ∿2% of the ^{131}I was lost as organic iodide. The Agx cartridge lost ∿3% of its ^{131}I as organic iodide. Previous losses were also ∿3%.

3.2 Test 2

Unfiltered Air

Length of Purge: 76 hours
Temperature: 75±3°F
Relative Humidity: 60±15%

		Original Cartridge		
	PF	CdI_2	IPH	Char
% Loss from each Component	11.8%	2.5%	1.1%	<1%
Form				
Particulate	17%	<1	<1	-
I_2	78%	100%	<1	-
HOI	5%	<1	45%	-
Organic	<1%	<1	50%	-

In this test, very little was lost from any of the components. That which was purged off, behaved very much as in Test 1, with the principal losses occurring to the particulate filter, the iodine purging off as elemental iodine. However, the loss from the filter with the unfiltered air purge was less than 1/5 that in test 1.

3.3 Speculation on Nature of the Losses in Purging.

Loss of radioiodine from the sampler components may be caused by one or more of three mechanisms. One is oxidation of the adsorbed iodine to I_2 or even to HOI when water vapor is present. Another is exchange, where an atom of stable iodine replaces a radioactive iodine atom. The last is revolatilization of the adsorbed iodine in its original chemical form.

The TEDA charcoal used for the filtered air test would remove the ambient iodine, ozone and other strong oxidants and most of the organic vapors in the lab air.

Oxidation of the particulate iodine to I_2 or exchanges with ambient iodine may be the major loss mechanism for the PF cartridge. When the air was filtered the amount of radioiodine lost from the PF in test 1, dropped by a factor of ∿9. Oxidation or exchange may also be the primary cause of the radioiodine loss from the CDI cartridge. Test 2 seems to indicate a different type of particulate iodine. The small amount of iodine listed as I_2 lost from the IPH may be HOI retained on the elemental iodine adsorber. The loss of HOI from the IPH can possibly be explained as revolatilization or simple exchange. The organic iodine loss from the IPH may likely be due to the formation of these iodides in the IPH media. This can be supported by the observation that ∿3% of the total radioiodine on the IPH was lost as organic iodine in both tests. We can offer no reasonable explanation for the loss of radioiodine from the AGX cartridge. It is possible that some unreacted organic iodide has slowly been purged from the cartridge.

4.0 Comparison of In-Plant and Lab Tests

In-plant efficiencies are determined from the dual bed tests.

CDI Media

	Inlet $\mu gl/m^3$	Temp. °F	%R.H.	R.T. (sec)	R.T. (hr.)	%Eff.
In Plant	10^{-8}-10^{-10} est.	105-120	<20	0.1-0.13	200-400	82%-91%
Lab	∿2(-6)	111	10	0.08-0.17	3	86%-93%

IPH Media

	Inlet $\mu gl/m^3$	Temp. °F	%R.H.	R.T. (sec)	R.T. (hr.)	%Eff.
In Plant	10^{-7}-10^{-8}	105-120	<20	0.1	360-430	>99
Lab	∿2(-5)	110	10	0.1-0.16	3	93-96%

AGX Media

	Inlet $\mu gl/m^3$	Temp. °F	%R.H.	R.T. (sec)	R.T. (hr.)	%Eff.
In Plant	∿10^{-7}	∿100	<20	0.16	210	99.4%
Lab	∿2(-5)	110	10-16	0.08-0.16	3	99.9%

4.0 Continued

In all cases the in-plant tests agreed well with the lab tests. Before the IPH tests were run, it was suspected that the 4-iodophenol impregnant might be slowly volatilized from the media under hot dry conditions. This is shown not to be a problem. If significant amount of 4-iodophenol were lost, the species fractions at this same condition would appear different between samples taken for 12 hours, 48 hours, and 400 hours. We have found this not to be the case.

VII. Comparison of Results With Other Investigators

The data from this study compare favorably, with one exception, with the work by Keller, et.al. described in Section II of this work, the one exception is the CDI. His reported efficiency for I_2 by CDI is >90%. The CDI efficiency, under the conditions we tested, is ∿85%. At the concentration levels of the tests, we never obtained a CDI efficiency of greater than 93%. Attempts were made to determine the reason for the lower efficiency. No cause was found. Even with the ∿84% efficiency of CDI for I_2, this sampler will give the required data for Phase II of the program.

The IPH results of this study while comparing well with Keller's data, do not compare well with the more recent information released by Kabat[15]. It was reported that the "Chemical reaction of HOI with the presently used impregnanta (including 4-Iodophenol) is slow". "Slow" is a relative term. Based upon our limited profile work, and at the flow rates tested, the IPH media retained >90% of the HOI on the first one-third of the one inch bed. Whatever reaction occurred,did so in ∿30 milliseconds. This is fast relative to the residence time in the bed. Certainly fast enough a reaction to be able to determine the HOI component in an air stream of radioiodine. Also, it was stated by Kabat that "4-Iodophenol impregnated alumina has a low efficiency for HOI adsorption when several hours sampling time is applied at low humidity conditions (<50% R.H.)". We find high HOI efficiencies (∿94%) for IPH at ∿10% R.H. for periods of 2, 6, 11, 48, and up to 432 hours. Furthermore Kabat has stated that "Adsorption of HOI on both 4-Iodophenol impregnated and non-impregnated alumina is negligible at 70% RH when sampling time exceeds 2 hours". Since non-impregnated alumina has not been tested for this study, no comment on its HOI efficiency can be made. However, the test data reported above at 90°F and 70% R.H. show an efficiency of ∿95%. We have no explanations for the differences in results. No experimental data or detailed test procedures were reported by Kabat.

VIII. Summary and Conclusions

A. Use of the Iodine Species Sampler

The lab test ranges of temperature (60° - 110°F) and humidity (10% - 90% R.H.) cover the anticipated sampling points fairly well. Two exceptions exist. First, some temperatures have run as high as 140°F inside of a turbine building. It is felt that this will not be a problem. Results reported above show adequate sampler performance for periods up to 18 days at 120°F. Secondly, relative humidity of ∿100% occurs at sampling points such as a gland-seal exhauster line. If possible, a sampler should be placed in a sampling line after the relatively small flow of the high humidity duct is mixed with a large air flow of lower relative humidity. If this is not possible the sampler and inlet lines should be heated to reduce the relative humidity to 80%-90%. This technique of heating the sampler has been used successfully at plants. The recommended use parameters for the present sampler are given in

A. Continued

Table 11. The media efficiencies for the species are given in Table 12.

Table 11

Recommended Use Parameters

For the Radioiodine Species Sampler

Temperature:	60° - 140°F
Relative Humidity:	10% - 90%
Residence Time:	0.1 - 0.17 sec
Air Sample Flow Rate:	0.47-0.80 ℓ/s

Table 12

Media Efficiencies

Species	CDI	IPH	AGX/CH
I_2	84±4%*	>98%	99±1%
HOI	∿4%	94±4%	99±1%
CH_3I	<.02%	<.02%	99±1%

* If the sampler is run at a residence time >0.17 sec the efficiency for I_2 collection on CDI would be 90±3%.

The results presented in Tables 11 and 12 show the sampler can be used in typical nuclear power plants to monitor the total gaseous releases of radioiodine. The use parameters do not rule out the sampler performing well outside these limits. They merely define the limit of adequate performance as defined by the testing.

B. Conclusions

Based upon the test results, the following conclusions are offered.

1.0 Radioiodine Species Sampler for Effluent Measurements

1) The radioiodine species sampler tested in this program will differentiate the known chemical forms of radioiodine in gaseous effluents for sampling periods of at least two weeks and for relative humidities up to 90% and temperatures of at least 120°F. A residence time of 0.1 second gives satisfactory differention.

2) There is no indication of imminent failure of the sampler to differentiate species at more severe conditions than those used in our testing. Based on our tests and those of others, relative humidity appears to be the most critical parameter.

3) Until such time as tests can be made which show the limits at which the sampler will fail to differentiate, it would be prudent to heat the incoming air and the sampler when used to sample streams with relative humidities greater then 90%. Heating will reduce the relative humidity. Examples of gas streams with very high related humidities are off-gas, gland seal exhaust and steam generator blow down vents.

B. RADIOIODINE REMOVAL EFFICIENCIES OF CHARCOAL ADSORBERS FOR VENTILATION EXHAUST AIR*

I. Introduction

On May 28, 1975, a sampling program was initiated at the Ginna nuclear power station to measure the radioiodine removal efficiencies of two charcoal adsorbers over an extended time period. Two installations were evaluated. One consists of 665 liters of charcoal in 32 trays each having dimensions of 72.4 cm. by 56.5 cm. and 5.1 cm. in depth. The installation which has no HEPA filters carries 1.33×10^5 liters/min. (4700 cfm), and the residence time of air in the charcoal is 0.3 seconds.

The other installation carries about 7.08×10^5 liters/min. (25,000 cfm) and has 3750 liters of charcoal in 168 trays each having dimensions of 67.3 cm. by 62.2 cm. and 5.1 cm. in depth. The installation contains HEPA filters in series before the charcoal adsorbers. The residence time of air in the charcoal is also 0.3 seconds.

The charcoal adsorbers in the small filter are changed periodically due to high pressure drop. They were replaced on June 6, 1975, which is at the beginning of the sampling program. The HEPA filters in the large installation are changed periodically due to high pressure drop, but the charcoal has not been changed since the filter was installed in June 1973.

Methods

Figure 2 shows the layout of two installations and the 6 sampling points used. Single tipped probes were used for sampling. To assure representativeness of sampling, a helium tracer was introduced at a known rate upstream of the sampling point and if the airflow rate in the duct computed from the measured helium concentration and the known release rate was the same as that measured by conventional techniques, using the standard pitot tube, the sampler was assumed to be taking a representative sample.

From May 28 to October 2, 1975, the sampling train consisted of a particulate filter (Flanders 700) followed by two charcoal adsorbers in series. A constriction was put in the line behind the charcoal and particulate filters and a small flow was bypassed through a 400 gram silica gel tower to measure tritium in the airstream. Nominal flow rates through the particulate and charcoal filters and the silica gel were 42.5 liters/min. (1.5 cfm) and .056 liters/min. (0.002 cfm) respectively. The second charcoal adsorber in the sampler was used for the purpose of measuring breakthrough of the first adsorber. Seldom was more than 1% of the iodine-131 found on the second adsorber. A layer of tell-tale silica gel was employed

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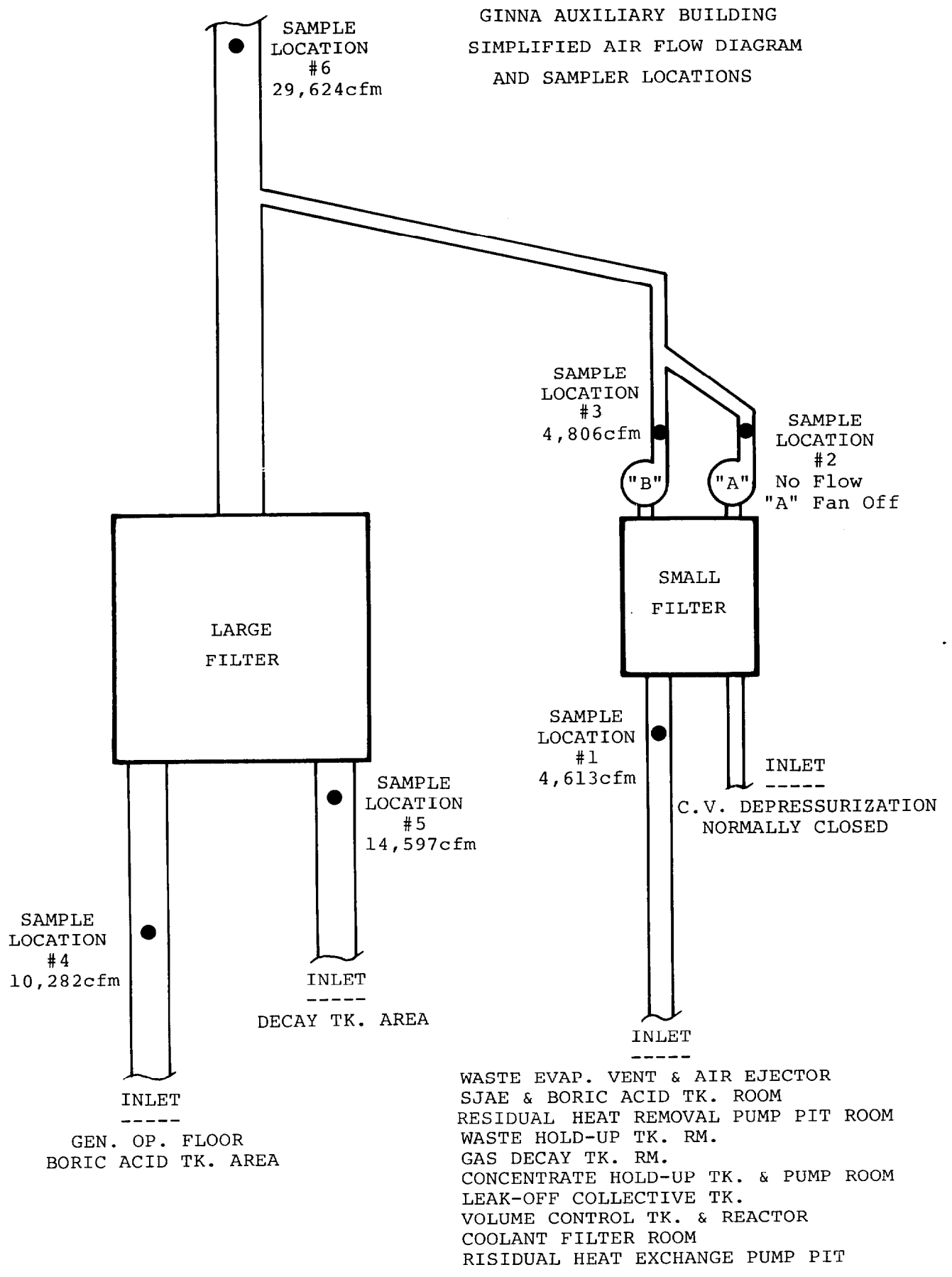
FIGURE 2


GINNA AUXILIARY BUILDING
SIMPLIFIED AIR FLOW DIAGRAM
AND SAMPLER LOCATIONS
SAMPLE LOCATION #6 29,624cfm
SAMPLE LOCATION #3 4,806cfm
SAMPLE LOCATION #2 No Flow "A" Fan Off
"B"
"A"
LARGE FILTER
SMALL FILTER
SAMPLE LOCATION #1 4,613cfm
INLET
C.V. DEPRESSURIZATION NORMALLY CLOSED
SAMPLE LOCATION #5 14,597cfm
SAMPLE LOCATION #4 10,282cfm
INLET
DECAY TK. AREA
INLET
GEN. OP. FLOOR
BORIC ACID TK. AREA
INLET
WASTE EVAP. VENT & AIR EJECTOR
SJAE & BORIC ACID TK. ROOM
RESIDUAL HEAT REMOVAL PUMP PIT ROOM
WASTE HOLD-UP TK. RM.
GAS DECAY TK. RM.
CONCENTRATE HOLD-UP TK. & PUMP ROOM
LEAK-OFF COLLECTIVE TK.
VOLUME CONTROL TK. & REACTOR
COOLANT FILTER ROOM
RISIDUAL HEAT EXCHANGE PUMP PIT

at the exit end of the silica gel tower to measure column saturation. This was never observed with any of the samplers.

On October 2, 1975, the particulate filter and total iodine sampler was replaced with the species sampler described in section A above. With the exception of two sampling periods from 11/25 to 12/29, species measurements were made until March 24, 1976. The reason for discontinuing species sampling in favor of total iodine sampling was the fact that we experienced difficulties with the IPH adsorber media. When the cause was found and rectified species sampling was resumed.

Iodine-131 was measured using a 4096 channel Ge(Li) spectrometer. Tritium was measured with a liquid scintillation detector. The average sampling duration ranged from 13 days to 25 days and averaged 17 days. Each measured concentration was corrected for decay from the end of the sampling period to the time of counting. Concentrations were also corrected for the decay during the finite sampling interval.

Decontamination factors for the small and large charcoal filter installations were calculated as follows.

$$\text{D.F. (small filter)} = C_1/C_2 \text{ (or } C_3),$$
$$\text{D.F. (large filter)} = (Q_4C_4+Q_5C_5)/(Q_6C_6-Q_2C_2 \text{ or } {}_3),$$

where C's are the concentrations and
Q's are the flow rates in ducts.

The subscripts refer to the sampling locations shown in figure 1.

Results

Table 13 shows results of the measurements of total iodine-131 and tritium.

Table 14 shows the results of the iodine-131 species measurements. In addition to the long duration measurements started on October 2, the results of a set of shorter duration species measurements made from September 3-5, 1975 are included for completeness.

Tables 15 & 16 summarize the calculations of the decontamination factors for the large and small filters respectively. They are listed in order of leapsed time since the charcoal was installed and the corresponding number of air changes experienced by the filters.

Discussion

As shown in Table 14 the results listed are concentrations (release rates) as measured on each adsorber. No corrections have been made for the efficiency of each adsorber for the various species. The reason for this is the uncertainty arising from unknown behavior of iodine-131 on particulate matter. In our other work for EPRI we have observed on one occasion that iodine-131 could be purged off the

TABLE 13 GINNA AUXILIARY BUILDING
^{131}I & TRITIUM RELEASES (μCi/sec)

	^{131}I	^{3}H
7/17/75 - 8/6/75		
#1 Inlet Sm. Filter	7.1±0.4(-4)	1.1±0.2(-1)
#2 "A" Fan Off & Dampers closed - no flow	--	--
#3 "B" Fan Outlet Sm. Filter	3.0±0.8(-6)	1.2±0.2(-1)
#4 Gen. Op. Floor	1.7±0.1(-4)	1.4±0.3(-1)
#5 Decay Tk. Area	3.7±0.2(-4)	1.2±0.2(-1)
#6 Outlet Lg. & Small Filters	5.4±0.3(-5)	4.0±0.8(-1)
8/6/75 - 8/19/75		
#1 Inlet Sm. Filter	7.9±0.4(-5)	1.1±0.2(-1)
#2 "A" Fan Off - No Flow	--	--
#3 "B" Fan Outlet Sm. Filter	1.5±0.3(-6)	1.2±0.2(-1)
#4 Gen. Op. Floor	2.6±0.3(-5)	1.3±0.3(-1)
#5 Decay Tk. Area	8.0±0.4(-5)	1.3±0.3(-1)
#6 Outlet Lg. & Small Filters	1.3±0.1(-5)	3.8±0.8(-1)
8/19/75 - 9/3/75		
#1 Inlet Sm. Filter	2.5±0.3(-4)	1.4±0.3(-1)
#2 "A" Fan Off - No Flow	--	--
#3 "B" Fan Outlet Sm. Filter	1.6±0.3(-6)	1.7±0.3(-1)
#4 Gen. Op. Floor	1.4±0.2(-5)	1.3±0.3(-1)
#5 Decay Tk. Area	6.3±0.7(-5)	1.8±0.4(-1)
#6 Outlet Lg. & Sm. Filters	9.7±1.0(-6)	4.6±0.9(-1)
9/5/75 - 9/18/75		
#1 Inlet Sm. Filter	2.4±0.1(-4)	1.1±0.2(-1)
#2 "A" Fan Off - No Flow	--	--
#3 "B" Fan Outlet Sm. Filter	3.1±0.5(-6)	1.2±0.2(-1)
#4 Gen. Op. Floor	8.2±1.3(-6)	9.6±1.9(-2)
#5 Decay Tk. Area	5.9±0.6(-5)	1.1±0.2(-1)
#6 Outlet Lg. & Sm. Filters	1.1±0.2(-5)	3.4±0.7(-1)
9/18/75 - 10/2/75		
#1 Inlet Sm. Filter	7.0±0.4(-5)	1.0±0.2(-1)
#2 "A" Fan Off & Dampers closed - no flow	--	--
#3 "B" Fan Outlet Sm. Filter	1.4±0.4(-6)	1.6±0.3(-1)
#4 Gen. Op. Floor	3.3±1.0(-6)	1.3±0.2(-1)
#5 Decay Tk. Area	3.9±0.2(-5)	1.5±0.3(-1)
#6 Outlet Lg. & Small Filters	5.5±1.7(-6)	4.5±0.9(-1)
10/2/75 - 10/16/75		
#1 Inlet Sm. Filter	5.1±0.3(-4)	1.2±0.2(-1)
#2 "A" Fan Off & Dampers closed - no flow	--	--
#3 "B" Fan Outlet Sm. Filter	1.3±0.9(-6)	1.2±0.2(-1)
#4 Gen. Op. Floor	8.9±0.8(-6)	8.4±1.7(-2)
#5 Decay Tk. Area	2.2±0.1(-4)	1.1±0.2(-1)
#6 Outlet Lg. & Small Filters	3.5±0.2(-5)	3.6±0.7(-1)

TABLE 13 (continued)

	^{131}I	^{3}H
10/16/75 - 11/5/75		
#1 Inlet Sm. Filter	6.6±0.4(-5)	1.9±0.4(-1)
#2 "A" Fan Off - No Flow	--	--
#3 "B" Fan Outlet Sm. Filter	1.6±0.5(-6)	9.7±1.9(-2)
#4 Gen. Op. Floor	5.0±1.2(-6)	6.2±1.2(-2)
#5 Decay Tk. Area	6.7±0.5(-5)	1.0±0.2(-1)
#6 Outlet Lg. & Small Filters	7.4±1.3(-6)	3.2±0.6(-1)
11/5/75 - 11/25/75		
#1 Inlet Sm. Filter	3.3±0.2(-4)	1.2±0.2(-1)
#2 "A" Fan Off - No Flow	--	--
#3 "B" Fan Outlet Sm. Filter	1.0±0.2(-6)	1.1±0.2(-1)
#4 Gen. Op. Floor	2.4±0.5(-6)	6.0±1.2(-2)
#5 Decay Tk. Area	4.4±0.7(-5)	1.2±0.2(-1)
#6 Outlet Lg. & Sm. Filters	9.8±1.6(-6)	3.3±0.7(-1)
11/25/75 - 12/11/75		
#1 Inlet Sm. Filter	1.1±0.1(-4)	1.3±0.3(-1)
#2 "A" Fan Off - No Flow	--	--
#3 "B" Fan Outlet Sm. Filter	4.7±1.4(-7)	1.4±0.3(-1)
#4 Gen. Op. Floor	1.5±0.4(-6)	9.5±1.9(-2)
#5 Decay Tk. Area	4.1±0.3(-5)	2.0±0.4(-1)
#6 Outlet Lg. & Sm. Filters	<8(-6)	5.5±1.1(-1)
12/11/75 - 12/29/75		
#1 Inlet Sm. Filter	1.2±0.1(-4)	2.4±0.5(-1)
#2 "A" Fan Off & Dampers closed - no flow	Changed Fans 12/22 - Averaged results of #2 & #3	
#3 "B" Fan Outlet Sm. Filter	1.5±0.1(-6)	1.9±0.4(-1)
#4 Gen. Op. Floor	1.2±0.3(-5)	8.9±1.8(-2)
#5 Decay Tk. Area	4.5±0.2(-5)	3.4±0.7(-1)
#6 Outlet Lg. & Small Filters	7.3±1.2(-6)	5.9±1.2(-1)
12/29/75 - 1/13/76		
#1 Inlet Sm. Filter	7.2±0.3(-3)	2.3±0.5(-1)
#2 "A" Fan	3.4±0.2(-4)	1.2±0.3(-1)
#3 "B" Fan Off & Dampers closed - no flow	--	--
#4 Gen. Op. Floor	9.9±0.5(-4)	1.3±0.3(-1)
#5 Decay Tk. Area	1.0±0.1(-2)	5.2±1.0(-1)
#6 Outlet Lg. & Small Filters	2.0±0.1(-3)	7.7±1.5(-1)
1/13 - 1/27/76		
#1 Inlet Sm. Filter	3.1±0.2(-3)	2.7±0.5(-1)
#2 "A" Fan - Changed Fans 1/22/76 - Averaged Results		
#3 "B" Fan Outlet Sm. Filter	1.6±0.1(-5)	2.4±0.5(-1)
#4 Gen. Op. Floor	1.4±0.1(-3)	1.2±0.3(-1)
#5 Decay Tk. Area	6.2±0.3(-4)	1.3±0.3(-1)
#6 Outlet Lg. & Small Filters	4.1±0.2(-4)	1.4±0.3(-1)

TABLE 13 (continued)

	^{131}I	^{3}H
1/27 - 2/13/76		
#1 Inlet Sm. Filter	2.5±0.1(-3)	2.2±0.4(-1)
#2 "A" Fan Off & Dampers Closed - no flow	--	--
#3 "B" Fan Out Sm. Filter	3.1±0.3(-5)	1.6±0.3(-1)
#4 Gen. Op. Floor	3.1±0.2(-4)	8.1±1.6(-2)
#5 Decay Tk. Area	5.4±0.3(-3)	4.7±0.9(-1)
#6 Outlet Lg. & Small Filters	1.5±0.1(-3)	1.3±0.2(1)*
2/13 - 3/3/76		
#1 Inlet Sm. Filter	1.7±0.1(-4)	1.8±0.4(-1)
#2 "A" Fan Off & Dampers Closed - no flow	--	--
#3 "B" Fan Outlet Sm. Filter	8.6±1.1(-6)	1.5±0.3(-1)
#4 Gen. Op. Floor	8.0±0.6(-5)	8.6±1.7(-2)
#5 Decay Tk. Area	3.0±0.2(-4)	2.3±0.5(-1)
#6 Outlet Lg. & Small Filters	6.4±0.6(-5)	4.5±0.9(-1)
3/3 - 3/24/76		
#1 Inlet Sm. Filter	5.5±0.3(-5)	3.6±0.7(-1)
#2 "A" Fan Off & Dampers Closed - no flow	--	--
#3 "B" Fan Outlet Sm. Filter	4.7±2.6(-7)	9.1±1.8(-2)
#4 Gen. Op. Floor	4.3±0.3(-5)	6.1±1.2(-2)
#5 Decay Tk. Area	4.9±0.3(-5)	1.5±0.3(-1)
#6 Outlet Lg. & Small Filters	1.9±0.2(-5)	3.4±0.7(-1)

*Believe this to be a sampling error.

TABLE 14 RESULTS OF ^{131}I CHEMICAL FORM MEASUREMENTS* AT GINNA

		9/3 - 9/5/75	10/2 - 10/16**	10/16 - 11/5**	11/5 - 11/25**
#1 Inlet Small Filter	PF	2.3%	.3%	.6%	--
	CdI_2	24.9%	4.0%	10.9%	1.7%
	IPH^2	57.4%	9.2%	--	.1%
	CHARCOAL	15.4%	84.3%	88.5%	98.2%
	TOTAL (μCi/sec)	4.1±0.3(-4)	5.1±0.3(-4)	6.6±0.4(-5)	3.3±0.2(-4)
#2 "A" Fan - Fan Off and Dampers Closed - No Flow					
#3 "B" Fan	PF	27.3%	33.7%	--	--
	CdI_2	--	28.4%	32.4%	--
	IPH^2	59.5%	--	--	--
	CHARCOAL	13.2%	37.9%	67.6%	100%
	TOTAL (μCi/sec)	5.3±2.8(-6)	1.3±0.9(-6)	1.6±0.5(-6)	1.0±0.2(-6)
#4 Gen. Op. Floor	PF	84.3%	--	--	--
	CdI_2	10.6%	13.3%	13.0%	--
	IPH^2	5.1%	--	17.8%	--
	CHARCOAL	--	86.7%	69.2%	100%
	TOTAL (μCi/sec)	8.6±7.6(-5)	8.9±0.8(-6)	5.0±1.2(-6)	2.4±0.5(-6)
#5 Decay Tank Area	PF	--	2.8%	1.8%	--
	CdI_2	17.1%	17.9%	25.4%	18.6%
	IPH^2	59.2%	.8%	16.2%	--
	CHARCOAL	23.7%	78.5%	56.6%	81.4%
	TOTAL (μCi/sec)	8.0±2.8(-5)	2.2±0.1(-4)	6.7±0.5(-5)	4.4±0.7(-5)
#6 Outlet Large & Small Filter	PF	--	--	--	--
	CdI_2	--	--	--	--
	IPH^2	--	--	--	--
	CHARCOAL	100%	100%	100%	100%
	TOTAL (μCi/sec)	6.9±4.3(-6)	3.5±0.2(-5)	7.4±1.3(-6)	9.8±1.6(-6)

*Values are ^{131}I measured on each adsorber in sampler. No corrections for the efficiencies of each bed for various chemical forms have been made.
**Efficiency of IPH media for HOI collection is suspect.

TABLE 14 (continued)

		12/29 - 1/13	1/13 - 1/27	1/27 - 2/13	2/13 - 3/3
#1 Inlet Small Filter	PF	.2%	.1%	.3%	1.6%
	CdI_2	6.5%	4.85%	9.7%	23.9%
	IPH^2	22.1%	7.63%	25.3%	38.4%
	CHARCOAL	71.2%	86.5%	64.7%	36.1%
	TOTAL (μCi/sec)	7.2±0.3(-3)	3.1±0.2(-3)	2.5±0.1(-3)	1.7±.09(-4)
#2 "A" Fan	PF	2.8%	Changed Fans 1/22/76 Averaged Results	Fan Off and Dampers Closed	Fan Off and Dampers Closed
	CdI_2	22.3%			
	IPH^2	48.7%			
	CHARCOAL	26.2%			
	TOTAL (μCi/sec)	3.4±0.2(-4)			
#3 "B" Fan -	PF	Fan Off and Dampers Closed	Had only char. on "B" Fan so % of Species could mislead	7.8%	8.6%
	CdI_2			7.9%	25.3%
	IPH^2			6.3%	20.9%
	CHARCOAL			88.0%	45.2%
	TOTAL (μCi/sec)		1.6±0.1(-5)	3.1±0.3(-5)	8.6±1.1(-6)
#4 Gen. Op. Floor	PF	.1%	.2%	.4%	--
	CdI_2	2.5%	2.7%	3.6%	6.3%
	IPH^2	7.9%	5.9%	14.4%	14.8%
	CHARCOAL	89.5%	91.2%	81.6%	78.9%
	TOTAL (μCi/sec)	9.9±0.5(-4)	1.4±.07(-3)	3.1±0.2(-4)	8.0±0.6(-5)
#5 Decay Tank Area	PF	.2%	.8%	1.2%	4.7%
	CdI_2	13.4%	22.0%	12.3%	36.3%
	IPH^2	57.5%	38.8%	40.7%	35.7%
	CHARCOAL	28.9%	38.4%	45.8%	23.2%
	TOTAL (μCi/sec)	1.0±0.1(-2)	6.2±0.3(-4)	5.4±0.3(-3)	3.0±0.2(-4)
#6 Outlet Large & Small Filter	PF	.8%	--	--	3.5%
	CdI_2	.8%	.1%	.2%	3.0%
	IPH^2	.8%	--	.4%	2.1%
	CHARCOAL	97.6%	99.9%	99.4%	91.4%
	TOTAL (μCi/sec)	2.0±0.1(-3)	4.1±0.2(-4)	1.5±.08(-3)	6.4±0.6(-5)

TABLE 14 (continued)

		3/3 - 3/24/76
#1 Inlet Small Filter	PF	1.0%
	CdI_2	10.0%
	IPH^2	27.2%
	CHARCOAL	61.8%
	TOTAL (μCi/sec)	5.5±0.3(-5)
#2 "A" Fan	PF	Fan Off and Dampers Closed
	CdI_2	
	IPH^2	
	CHARCOAL	
	TOTAL (μCi/sec)	
#3 "B" Fan	PF	51.8%
	CdI_2	48.2%
	IPH^2	--
	CHARCOAL	--
	TOTAL (μCi/sec)	4.7±2.6(-7)
#4 Gen. Op. Floor	PF	--
	CdI_2	5.5%
	IPH^2	47.6%
	CHARCOAL	46.9%
	TOTAL (μCi/sec)	4.3±0.3(-5)
#5 Decay Tank Area	PF	--
	CdI_2	22.7%
	IPH^2	42.2%
	CHARCOAL	35.1%
	TOTAL (μCi/sec)	4.9±0.3(-5)
#6 Outlet Large & Small Filter	PF	--
	CdI_2	--
	IPH^2	--
	CHARCOAL	100%
	TOTAL (μCi/sec)	1.9±0.2(-5)

TABLE 15 DECONTAMINATION FACTORS FOR IODINE - 131 ACROSS THE LARGE FILTER (∿25,000 cfm)

Exposure Time (d)	10^8 Air Changes	D.F. Part.	CdI_2	IPH	Char.	Total
730	2.1	NS	NS	NS	NS	2.0
743	2.1	NS	NS	NS	NS	11.0
758	2.2	NS	NS	NS	NS	12.0
778	2.2	NS	NS	NS	NS	11.0
791	2.3	NS	NS	NS	NS	9.5
816	2.3	NS	NS	NS	NS	9.5
818	2.3	>37	>4.6	>13	2.8	100.0
831	2.4	NS	NS	NS	NS	8.8
845	2.4	NS	NS	NS	NS	10.0
859	2.5	>6.2	>20	>0.9	5.2	6.8
879	2.5	>1.2	>9.0	>6.0	6.5	12.0
899	2.6	(1)	>4.1	(1)	4.3	5.3
915	2.6	NS	NS	NS	NS	6.0
933	2.7	NS	NS	NS	NS	9.9
948	2.7	3.2	(2)	(2)	2.0	6.7
962	2.7	>6.8	>85	>160	3.8	5.1
979	2.8	>65	1300	730	1.8	4.1
998	2.8	9.3	>55	> 60	2.4	7.0
1019	2.9	(1)	>14	>21	1.9	5.0
Average		>18	>190	>140	3.4	13.0

* Both the inlet and outlet concentrations were undetectable
** The quantity of iodine-131 measured at the outlet of the small filter was greater than that measured for the total quantity

TABLE 16 DECONTAMINATION FACTORS FOR IODINE - 131 ACROSS THE SMALL FILTER (4,700 cfm)

Exposure Time (d)	10^8 Air Changes	D.F.				
		Part.	CdI_2	IPH	Char.	Total
(1)	(1)	NS	NS	NS	NS	50
26	0.075	NS	NS	NS	NS	180
41	0.12	NS	NS	NS	NS	250
61	0.18	NS	NS	NS	NS	248
74	0.21	NS	NS	NS	NS	54
99	0.29	NS	NS	NS	NS	167
101	0.29	6.7	>200	75	90	77
114	0.33	NS	NS	NS	NS	70
128	0.37	NS	NS	NS	NS	54
142	0.41	3.4	54	>240	870	405
162	0.47	>2.7	14	>1.0	53	43
182	0.52	>1	> 28	>1.7	320	333
198	0.57	NS	NS	NS	NS	238
216	0.62	NS	NS	NS	NS	87
231	0.67	1.5	6.2	9.4	57	22
245	0.71	NS	NS	NS	NS	200
262	0.75	3.1	96	320	59	82
281	0.81	3.7	19	36	16	21
302	0.87	2.3	24	> 75	>170	122
Average		>3.1	> 55	> 95	>200	142

* Charcoal adsorbers changed after 9 days of a 22 day sampling period

particulate filter with clean room air and be caught on the CdI_2 adsorber. On two other occasions we have observed no purging of iodine-131 from the particulate filter when treated the same way. As will be seen below, iodine-131 on particulates was probably important in determining the effectiveness of the small installation. In this work efficiency corrections would make a relatively minor impact on the reported release rates, and they have no effect on the observations made of the effectiveness of the charcoal adsorbers being tested.

As pointed out in Table 14, the efficiency of the IPH media was suspect for the first three long duration sampling periods. Lab tests showed that the efficiency for the HOI species was from 30% to 50% during that period. This had no effect on the iodine-131 on particulates or on the CdI_2, but most likely increased the apparent organic fraction. The total iodine-131 reported in Table 13 for these periods was uneffected.

The measurements of tritium provided a continuing check on the quality of the sampling. The charcoal adsorbers should have little or no effect on the tritium concentrations and one would expect the D.F. calculated for tritium to be 1. The average tritium D.F. for the small filter was 1.26 with a standard deviation of the mean equal to 0.18. This D.F. is not significantly different than 1.0 (X=.05). The average D.F. and standard deviation of the mean for tritium for the large filter was 0.90 and 0.038 respectively. This D.F. is significantly different than 1(x = .0125) and there may be a bias in the sampling which would give slightly lower D.F. for iodine-131 than were real. On the whole however, we believe that the tritium measurements tend to verify the effectiveness of the sampling for iodine-131.

The reason for the many "greater than" symbols in Tables 15 and 16 is the fact that the I-131 activities on the particulate filter, the CdI_2 adsorber, and IPH adsorber were often less than our detection limit. In some cases radioiodine was not detectable at the inputs. The low concentrations undoubtly add to the observed variability in the calculated D.F.s.

None-the-less, it is clear from Table 15 that the D.F. for total iodine-131 and the organic fraction decreased with time. The low concentrations preclude such observation for the particulate, CdI_2 and IPH fractions. It is apparent however, that for the large filter, the D.F.s for these forms were much higher than the D.F.s for organic iodine. This is what one might expect. Table 16 shows the opposite for the small filter. The average D.F. for the organic fraction was much higher than that for the other more reactive iodine species. We believe that the low D.F. for iodine-131 on particulates is due to the penetration of the filter by particulates. As pointed out, the small filter has no HEPA filters. The lower D.F.s for the elemental and HOI forms may be due to the purging of the iodine-131 off the particulate filter in the sampler after collection.

To put the decrease in the D.F.s for organic and the total iodine with time into perspective we have compared our results to

those reported by Collins, et al[1]. Their "accelerated aging" tests for organic iodine showed the following relationship between filter performance and the number of air changes experienced by the filter: (The air they used was regular laboratory air).

$$\text{Log}(\text{D.F./R.T.}) = \log\ (\text{D.F./R.T.})_o\ e^{-r\ (\text{A.C.})}$$

where D.F. = Decontamination factor
R.T. = Residence time
A.C. = Number of 10^8 air changes
r = Constant

Their value for r was about 0.69 for tests with KI and TEDA Charcoal.

The data for total and organic iodine-131 in tables 15 & 16 were fit to exponential curves of the type shown above and the results were as follows:

	$\log(\text{D.F./R.T.})_o$	r	Coeff. of Determination
Large Filter*			
Total	5.9	0.57	0.61
organic	5.9	0.67	0.89
Small Filter *			
Total	5.8	-1.8	0.13
organic	11.6	-2.4	0.29

For the large filter installation the rate of decrease in performance for organic iodine with exposure is remarkably similar to that found by Collins, et al[1]. The very good agreement is considered fortuitous, but it does support the form of their expression for the decrease in performance of impregnated charcoal for collecting organic iodine with continued exposure. The rate of decrease in performance for total iodine-131 was less than that for organic iodine-131. This indicates that the ability of the filter to collect the other, more reactive forms, has not decreased as fast.

The fit to the exponential curve was not nearly as good for the small filter as evidenced by the low coefficient of determination. This is due to the much higher variability in the data. Some of the variability is due to experimental error and the relatively high D.F.'s encountered.

The performance of the small filter for organic iodine appears to have decreased faster than that of the larger filter. This could also have happened in the early stages for the large filter or it could be due to accelerated poisoning by materials not caught on HEPA filters. We have no way of knowing at this point. As for the large

*The short duration sample for 9/3-9/5/75 was not used in the curve fitting nor were the results from the first sampling period 5/28-6/19 used. The 9/3-9/5 sample had an unusually high fraction of particulate and elemental iodine. The 5/28-6/19 sample gave unusually low D.F.values and there may have been an experimental error.

filter, the decrease in performance for total-131 was less than for organic.

We plan to continue these measurements into July 1976.

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DISCUSSION

WILHELM: How much elemental iodine was adsorbed on the aerosol filters and how can you distinguish between elemental iodine and particulate iodine on your aerosol filters?

EMEL: It is very difficult to distinguish between the elemental and the truly particulate radioiodine on the sampler. Some of the radioiodine retained on the aerosol filter is converted to elemental iodine and removed from the filter by air purging. This was shown in the purge tests in Section VI of the paper. The amount of elemental iodine on the filter will vary depending on the sampler location in the plant. The lab tests did indicate a few per cent of the elemental iodine was retained on the aerosol filter used in the tests.

KABAT: This is a comment on paragraph VII of this paper. The large discrepancy in HOI adsorption efficiencies reported in ref. 15 and in this paper, is due to a different quality of alumina used in these two experiments. Alumina supplied by Fisher - Scientific was used in the experiment described in ref. 15. This alumina was highly efficient for water vapour adsorption. Therefore, the measured efficiency for HOI absorption was very low at humidity levels exceeding 70%. Six sets of the sampler described in this paper were purchased from SAI and recently tested in our laboratory. The measured HOI adsorption efficiency was significantly higher than the value reported in ref. 15 but the performance of two sections of the sampler (I_2 and HOI absorbents) still did not fulfill our requirements. Further, I suggest that the residence time of HOI for its chemical reaction with 4-iodophenol, be in the order of one hour rather than approximately 30 milliseconds as given in this paper. I believe that the physical adsorption of HOI on alumina, preceeding its chemical reaction with 4-iodophenol, is the basic factor controlling the process of HOI collection on this material .

EMEL: The substrate for the 4-iodophenol coating and the Fisher alumina (which turns out to be Alcoa F5) contains about 12 weight per cent calcium fluoride and it dosen't work worth a darn, as we indicated in the paper. We stumbled across it at first. The original paper said "activated alumina", therefore, we immediately went out and bought activated alumina. Activated alumina can be any of three or four different types. The type that works is Alcoa F1, a crystal form of alumina.

OPERATING EXPERIENCE WITH THE TESTING OF IODINE ADSORBERS ON THE AIR CLEAN UP SYSTEMS OF THE BELGIAN PWR POWER PLANTS.

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Abstract.

The in situ test method of iodine adsorbers used in France and Belgium has been developed by the French Atomic Energy Authority (CEA). Iodine 131 (in the form of elemental iodine or as methyl iodide) is injected in the ventilation duct up-stream to the adsorber ; the filter decontamination factor (DF) is derived from up-stream and down-stream samplings.

The main results obtained on Belgian plants are given considering two view points : acceptance of the installation and periodical testing. The results obtained are discussed in terms of :

- comparison of DF obtained by in situ and by laboratory measurements on activated carbon samples ;
- effect of air flow rate and relative humidity of the air flow through the adsorber ;
- determination of ventilation air flow from measurement of injected versus retained iodine as a possible cross check ;
- ageing of tested adsorbers.

This technique that has been widely tested for several years is particularly interesting as it allows determination of the whole adsorber conditions at the time of the tests and also because it yields a lot of valuable supplementary information.

1. Introduction.

For some years now, the gaseous effluents of nuclear power plants have been equipped with filtration systems for radioactive particulates that can originate after an accident as well as during normal plant operation. To complete these filtration systems an iodine 131 trapping on activated carbon impregnated with potassium iodide or triethylenediamine is used to improve the efficiency for the most penetrating iodine forms - in particular methyl iodide.

However, one essential problem is the ageing of the activated carbon : in fact it is established that permanently in service adsorbents as well as normally by-passed adsorbents age, resulting in a reduction of their efficiency with time.

As it is not possible to precisely predict what the ageing will be, it seems absolutely necessary to test these adsorption units initially and periodically to assure that their efficiency is satisfactory and in any case, higher than the safety requirements.

Many test conceptions can be envisaged. In parallel with a permanently used adsorption unit, one or more samples of the same batch as the main adsorbent can be installed. These samples are then periodically tested in a laboratory to determine the state of the adsorbent. These tests must however be accompanied by a system leak test to verify that no unacceptable leaks appear through or around the installed cells.

This is the solution used in the United States where the representative samples are periodically tested in a laboratory with methyl iodide and in some cases with molecular iodine, whilst the leak test is carried out with freon (1)(2). This solution presents nevertheless the disadvantage that the actual efficiency at a given moment of the whole installed filtration system is not determined.

Another answer consists of testing periodically in situ the whole installed system with methyl iodide and/or with molecular iodine. This method has the advantage of giving an idea of the actual state of the whole system - adsorbent and possible leaks - at the moment when the test is performed. This last solution seems to be presently preferred in Europe (3),(4),(5) and has been utilized up to now in the Belgian nuclear power plants. In addition to these periodical tests, it is possible to install in parallel with the adsorption unit one or more representative adsorbent samples subjected to regular laboratory tests : in this way, some supplementary information on the state of the adsorbent can be obtained (3),(4),(5).

In the present paper, we intend to give a résumé of the utilized technique, and also the conclusions obtained from 70 in situ tests carried out during the years 1974 to 1976 in the Belgian nuclear power plants.

2. In situ test technique.

The details of the iodine and methyl iodide injection and sampling devices have already been described elsewhere (5). We shall therefore only briefly recall their main features.

2.1. Molecular iodine or methyl iodide injection.

Molecular iodine is obtained by isotopic exchange between ^{131}I Na and $^{127}I_2$; in this case, a negligible amount of methyl iodide is formed. Methyl iodide is obtained by the reaction of methyl sulfate on the sodium iodide :

$$2\ ^{131}I\ Na + [CH_3]_2\ SO_4 \longrightarrow 2\ ^{131}ICH_3 + Na_2SO_4.$$

Either of these generation reactions take place directly in situ with the same device.

The whole generation and injection device (cfr. figure 1) is actuated by an air trump in glass especially designed for this use, which maintains the injection line in depression with regard to the atmosphere of a protective glove box, itself in depression with regard to the outside.

This system which we have used for several years is perfectly safe and we have never had any contamination incident. We note a low internal contamination on the glove box due to successive dismantlings and rebuildings when a series of tests have been performed:the adsorption on the carbon cartridge between the glove box and the outside prevents in this case a contamination of the ambient air.

2.2. Sampling device.

The samples, up-stream and down-stream of the adsorber, are taken with the device represented in figure 2. This device generally includes two carbon beds of 50 mm depth, but may accomodate as many supplementary beds as necessary. Each carbon bed is packed in the laboratory with a vibrating machine and the charcoal is maintained in place with springs.

The instantaneous sample flow is measured by the depression in a calibrated venturi tube. The air velocity through the sample is adjustable and lies in normal operation between 25 and 30 $cm.s^{-1}$.

Figure 3 gives a scheme of the typical arrangement for testing an installed adsorber bank.

To obtain representative samples in a homogeneous gaseous stream, the up-stream sample is taken near the adsorption unit, at a distance at least equal to 10 duct diameters from the injection point, whilst the down-stream sample is also taken at an equivalent distance of the adsorption unit. This arrangement seems essential since we want to determine the actual efficiency of the whole system with no influence of possible local defects. When the main adsorption unit can be by-passed, it is also desirable to include the by-pass valve between the up-stream and the down-stream sampling point. Indeed, we have frequently noted that the efficiency of an air cleaning system in this case is limited by the leak through the valve by-passing the trap, and not by the performance of the adsorbent itself.

3. In situ test procedure.

At least six hours before each test, the adsorption unit is put in operation to assure that the charcoal has reached the hygrometric equilibrium with the air passing through the bed.

The relative humidity of the air is measured before the test in the ventilation duct just up-stream and down-stream to the trap to determine the relative humidity appearing at the adsorbent level. On some units, especially on those preceded by heaters, we have noted that the air temperature (and hence the relative humidity) can vary widely from one point to another in the ventilation duct.

In parallel, we perform a flow measurement by means of a Pitot tube or a heated wire anemometer to estimate the residence time during the test.

The injection phase of the test lasts thirty minutes. The amount of iodine 131 to be injected is a function of the ventilation flow, of the highest efficiency sought to be measured and of the counting sensitivity. So, an activity of $3\ 10^{-5}$ Ci is sufficient to determine an efficiency of 1,000 with a ventilation flow of 20,000 $m^3.h^{-1}$ since the minimum detectable activity on our equipment reaches $5\ 10^{-12}$ Ci (sampling corresponding to 3 $m^3.h^{-1}$). With this method, the testing of air cleaning systems with very high ventilation flows does not provide any problems.

After the injection phase, sampling is still performed during one hour to take into account a possible desorption.

The countings are performed in the laboratory, by means of γ spectrometry, to prevent any interference with other artificial or natural radioisotopes (^{214}Pb for example, originating from the decrease of the radium emitted by the concrete of the buildings).

Taking into account the time to perform the test itself, to install the test equipment and to dismantle it, it is possible for two persons to carry out three tests a day.

4. Brief description of the tested systems.

All the tests, used as a basis for this study, have been performed on the air cleaning systems of the Doel 1 and 2 and Tihange 1 Belgian nuclear power plants.

The Doel power plant is a twin unit Westinghouse type PWR plant of 2 x 390 MWe ; the Tihange power plant is a Westinghouse type PWR plant of 870 MWe. These two plants have a double containment : in accident conditions, a depression is maintained in the space between primary and secondary containment

where the air is filtered both in closed loops and before extraction. There are no adsorption systems located inside the primary containment which have to operate in LOCA conditions. These power plants were put in operation in 1974 and 1975.

Among the tested adsorber banks, we have principally :
- the filtration systems of the atmosphere inside the space between the two containments,
- the filtration systems of the air extracted from this space in order to maintain it in depression,
- the filtration systems on the extraction of the auxiliary building, especially the spent fuel pool hall,
- the filtration systems of the control room and emergency plan room air.

On the whole, we have performed tests on 22 distinct filtration units. These units include prefilters, HEPA filters and iodine adsorbers.

The iodine adsorber cells installed in these units have been manufactured by SOFILTRA POËLMAN with activated charcoal impregnated with 1 % potassium iodide. Initially, the adsorbent beds were 25 mm deep with an air velocity of 0.3 $m.s^{-1}$. Very rapidly, measured efficiencies appeared low, sometimes insufficient, and the ageing process very fast. They have been progressively replaced first by 50 mm deep cells filled with coconut charcoal impregnated with potassium iodide, and with a nominal air velocity of 0.4 $m.s^{-1}$, afterwards by 50 mm deep cells filled with carboniferous charcoal with the same impregnation but with a nominal air velocity of 0.3 $m.s^{-1}$.

All the tested air cleaning systems are not in service during the normal operation of the plant. In the space between the two containments, the fans are normally not in service but are automatically put in operation after an accident. The other filtration systems are normally by-passed : only on high activity alarm signals, the by-pass valves close and the filtration systems are put in service. Consequently, the expected and observed ageing is essentially a static ageing, the operation time being practically limited to the periodical tests of the system.

5. Discussion of the results of the tests.

5.1. Comparison of the efficiencies obtained by in situ measurements and by laboratory measurements.

The apparent residence time of the air in the adsorbent directly influences the final efficiency : in practice now, none of the filtration systems installed in a power plant operate at the nominal flow for which the cells have been designed. To allow a comparison of results obtained on different units, we shall express them in the form of the index of performance, following the notation of Collins et al. [6] :

$$K = \frac{\log DF}{t}$$

where DF is the decontamination factor and t the residence time of the gas in the charcoal bed.

Although strictly, with constant residence time, the index of performance K is a function of the velocity of the air passing through the bed, we have neglected this variation in a first approach , the air velocities generally being between 20 and 35 $cm.s^{-1}$.

A sample of each activated carbon batch with which the adsorption units are filled, is subjected to laboratory tests, in order to determine the removal efficiency for molecular iodine and for methyl iodide. The efficiency for methyl iodide is determined at different relative humidities between 40 and 95 %. We have thus at our disposal the curve representing the index of performance K as a function of the relative humidity (cfr. figure 4).

On the same figure, we have drawn the values of the K index for methyl iodide, measured in situ by means of the above mentioned method.

With regard to the in situ measured K values below the values foreseeable by the laboratory tests (on figure 4, indicated by a circle with a cross), the inspection of the corresponding units have showed that the by-pass valves were not fully air-tight : hence, the efficiency of the whole system,by-pass valve included, is considerably lower than the removal efficiency of the activated carbon. It appears thus that this testmethod allows one, to a certain extent, to distinguish between a by-pass leak and a penetration through the bed.

Concerning the other K values (on figure 4 indicated by a circle), contrary to what should logically be expected, they are all higher than the values foreseeable by the laboratory tests. Several assumptions can be advanced to explain this phenomenon.

a) An error in the in situ measurement of the relative humidity of the air or of the air flow : it seems however unlikely that errors, systematically in the same direction appear in the measurement of these parameters.

b) The adsorbents have not reached the hygrometric equilibrium with the air passing through the beds. To prevent this lack of equilibrium, we have taken the precaution to put the adsorption units in operation at least 6 hours before the tests are carried out.

c) A certain amount of the injected iodine is adsorbed on the equipment other than the carbon adsorber, between the up-stream and the down-stream sampling points. We do not measure any activity retained by the absolute filter of the up-stream sampler. Thus, the injected iodine does not appear in the form of aerosols : it is therefore unlikely that the HEPA filters installed in the filtration systems remove a great deal of the methyl iodide. In addition, the adsorption on the ventilation ducts could only explain partially the observed differences of efficiency (cfr. § 5.2).

We have not performed such a comparison of the measured efficiencies for molecular iodine because we have not for the moment many experimental results. In addition, the removal efficiency of the activated carbon for molecular iodine is very high. Therefore, the in situ tests with molecular iodine demonstrate predominantly possible small by-pass leaks rather than a penetration through the activated carbon bed.

5.2. Cross check of the ventilation air flow by the iodine balance.

Knowing the total injected iodine activity, the sampled activity up-stream the adsorber and the sample flow, it should be possible to determine the air flow passing through the adsorber unit : thus, the efficiency of the system and the ventilation air flow could be verified by one unique test.

In practice, we have established that relative important differences appear between the air flow measured with the Pitot tube and the air flow calculated by the iodine balance.

If the injection point is not too distant from the up-stream sampling point, we have obtained cross checks of the measured air flow with the air flow calculated by the iodine balance, with a spread whose mean square root is 25 %.

When the injection point is more distant from the up-stream sampling point, we have observed that even during the methyl iodide tests, an important amount of injected iodine settles on the ducts. So, on a duct about 70 m long and 0.6 m^2 section, including 4 elbows at 90° and with an air flow of 6,000 $m^3.h^{-1}$ (gas velocity of 2.8 $m.s^{-1}$), we have observed that on average about 40 % of injected methyl iodide has deposited. During the tests performed with molecular iodine, about 70 % of the injected activity has deposited on this duct.

Consequently, in the present position, the cross check of the measured air flow with the air flow calculated by the iodine balance, is not perfectly realized : it can only give us an indication that the test has been well performed.

5.3. Adsorber ageing for methyl iodide.

From experimental measurements carried out on impregnated carbon, L.R. Taylor and R. Taylor [7] have proposed a relationship allowing calculation of the static as well as the dynamic ageing of impregnated carbon for methyl iodide :

$$\log_{10} K_t = \log_{10} K_o - 0.3\ 10^{-8}\ N - 1.3\ 10^{-3}\ t$$

where :

K_o = index of performance mentioned above at the start of ageing,

K_t = index of performance after t weeks ageing,

$$N = \frac{\text{total volume of gas passed through the bed}}{\text{geometric volume occupied by charcoal granules}},$$

t = age in weeks.

We have tried to compare the in situ observed ageing with the ageing foreseen by this relationship. To compare the in situ measurements, we have normalized the results at the same relative humidity. To do this, we have used the curves, representing the efficiency in terms of relative humidity that have been determined by laboratory tests (cfr. figure 4).

Taking into account that the tested filter banks are normally out of service, the observed ageing will essentially be a static ageing : we have verified that, under these conditions, by applying the relationship of L.R. Taylor and R. Taylor, the dynamic ageing must be negligible with regard to the static ageing for all the tested units.

The values used result from efficiency tests performed in situ on 9 adsorber banks ; the time between the successive tests has varied from 1 to 1.5 years for the different units. The results are presented in table 1.

We have observed that the ageing appearing on the adsorber units of the Doel power plant as well as those of the Tihange power plant is faster than the ageing foreseen by this relationship. However, a relatively important dispersion appears between the observed values of this ratio.

Taking into account
a) the limited amount of measurement results that we have obtained in situ on aged adsorber units,
b) the fact that these results have been obtained on recent plants where it cannot be excluded that some poisoning could occur,
c) the uncertainties introduced by the normalisation at a same relative humidity, we think it is however premature to draw definite conclusions about the velocity of the ageing process on adsorption units installed in power plants.

6. Conclusions.

In situ tests of iodine adsorption systems are quite feasible with labelled methyl iodide and can be performed without great inconvenience.

The main conclusions of these tests have shown that :
- the efficiencies obtained in situ seem to be appreciably higher than can be deduced by laboratory tests carried out on representative samples ;
- the ageing appears to be faster than expected. In the future, to increase the lifetime of the adsorbers, it would be desirable to increase the residence time and/or decrease as much as possible the relative humidity of the air passing through the adsorber.

This technique which permits a gross test takes into account simultaneously, in the measurement of decontamination factors, all the parameters which influence finally the efficiency of the air clean up systems.

References.

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(6) D.A. Collins, L.R. Taylor and R. Taylor "The development of impregnated charcoals for trapping methyl iodide at high humidity" TRG report 1300 (W) 1967.

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TABLE 1. AGEING OF IODINE ADSORBERS

Adsorber unit	Time between the two tests	Measurements during the tests			Normalisation		Time foreseen by the Taylor relationship to obtain the same ageing	Ratio of the observed ageing by the ageing foreseen by the Taylor relationship
		flow	relative humidity	K	relative humidity	K		
N°	weeks	$m^3.h^{-1}$	%	-	%	-	weeks	-
1	72	7.500	56	14,7	79	6,1		
		6.500	79	1,73	79	1,7	427	5,9
2	72	7.500	58	17,6	83	6,8		
		6.300	83	3,57	83	3,6	212	2,9
3	80	7.500	57	27,3	74	15		
		6.400	74	3,51	74	3,5	486	6,1
4	69	4.000	48	9,0	55	6,9		
		4.000	55	1,1	55	1,1	613	8,9
5	77	36.500	53	11,8	33	25		
		36.500	33	4,6	33	4,6	565	7,3
6	58	4.080	62	11,4	33	30		
		4.080	33	5,2	33	5,2	585	10
7	58	3.560	58	11,3	37	23		
		3.560	37	7,4	37	7,4	378	6,5
8	58	1.000	65	10,4	90	4,5		
		120	90	3,2	90	3,2	114	2,0
9	58	830	65	11,5	86	5,7		
		120	86	1,5	86	1,5	446	7,7

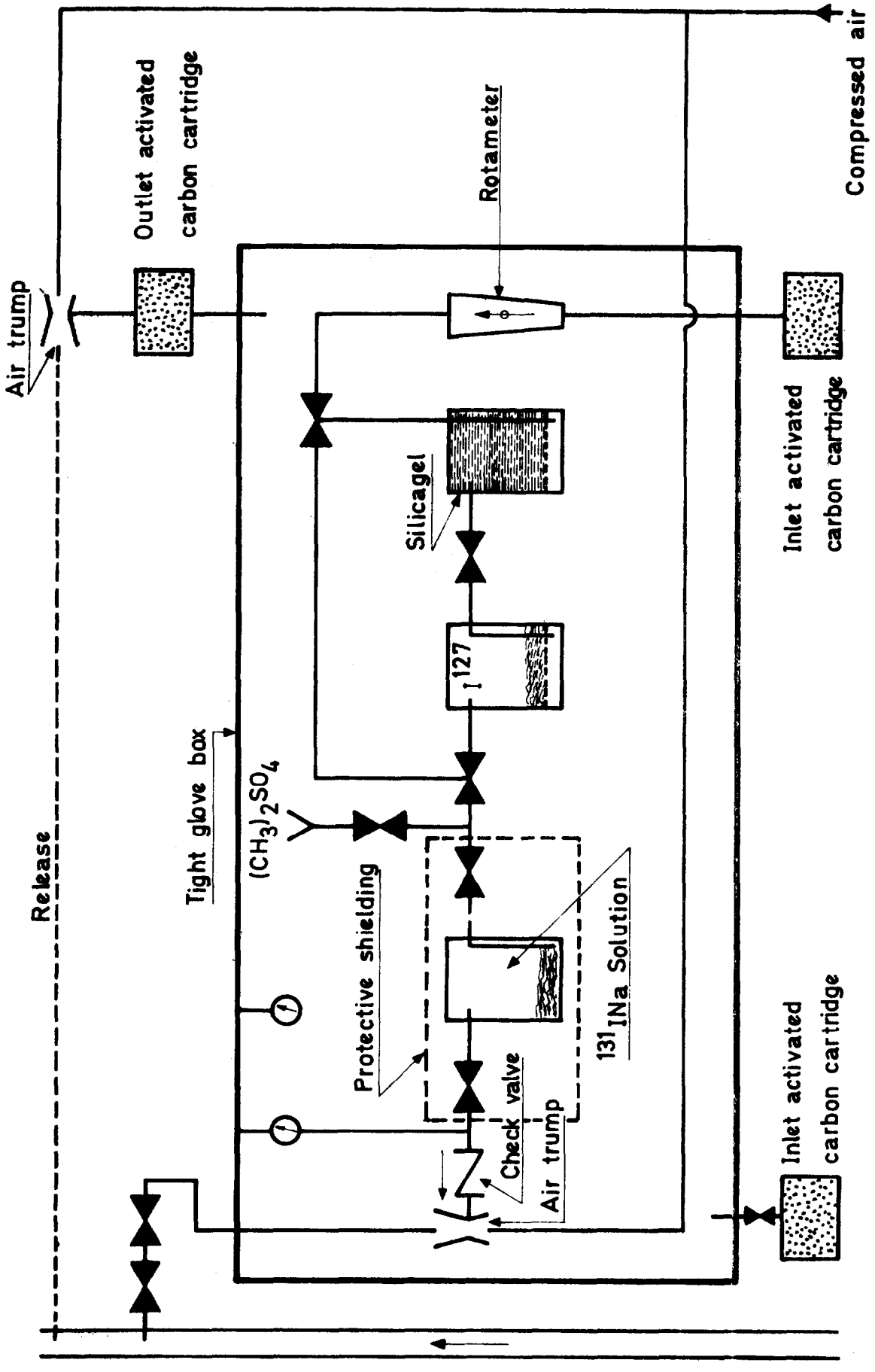

FIGURE 1: Injection device

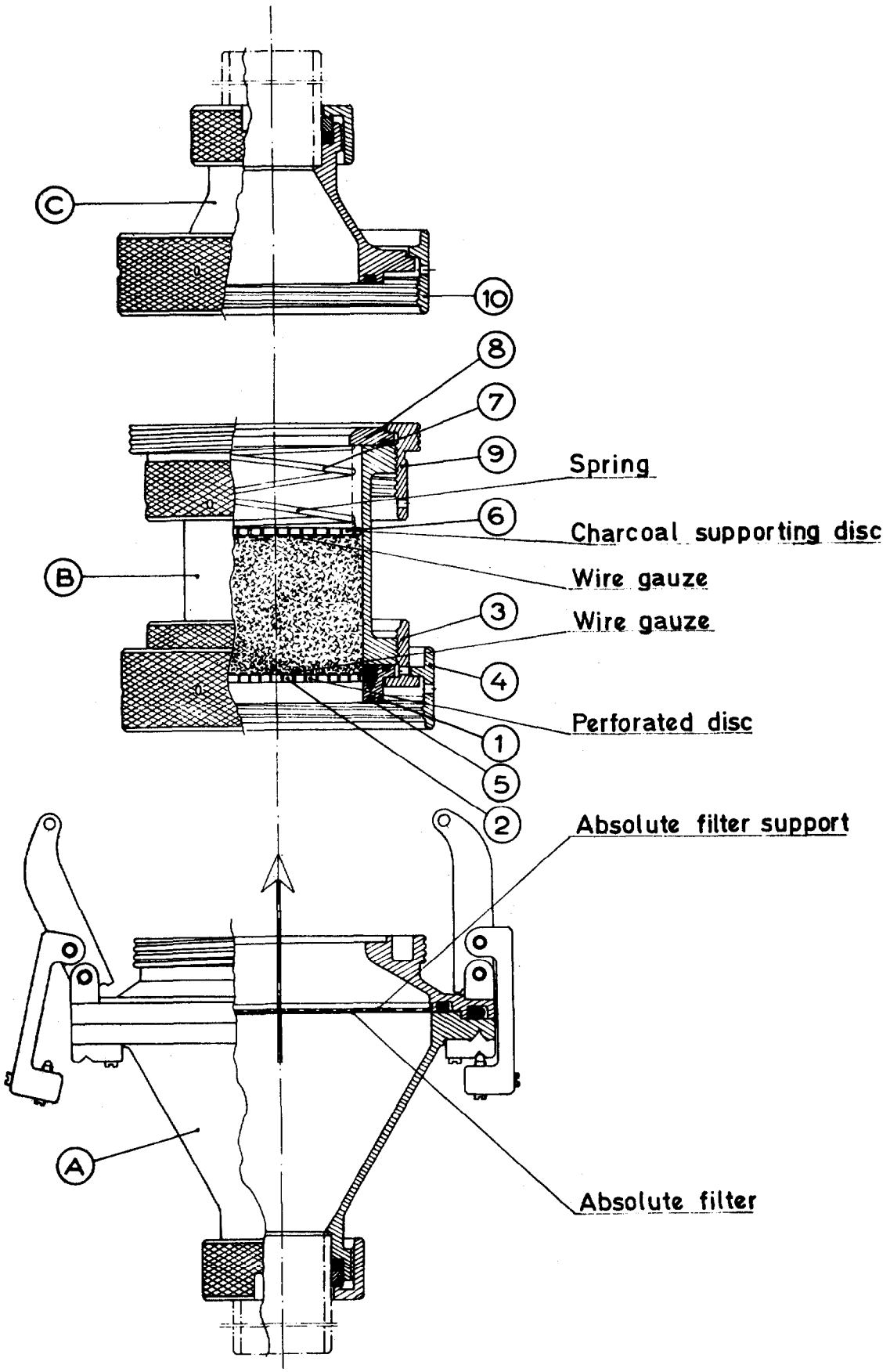

FIGURE 2 : Sampling device

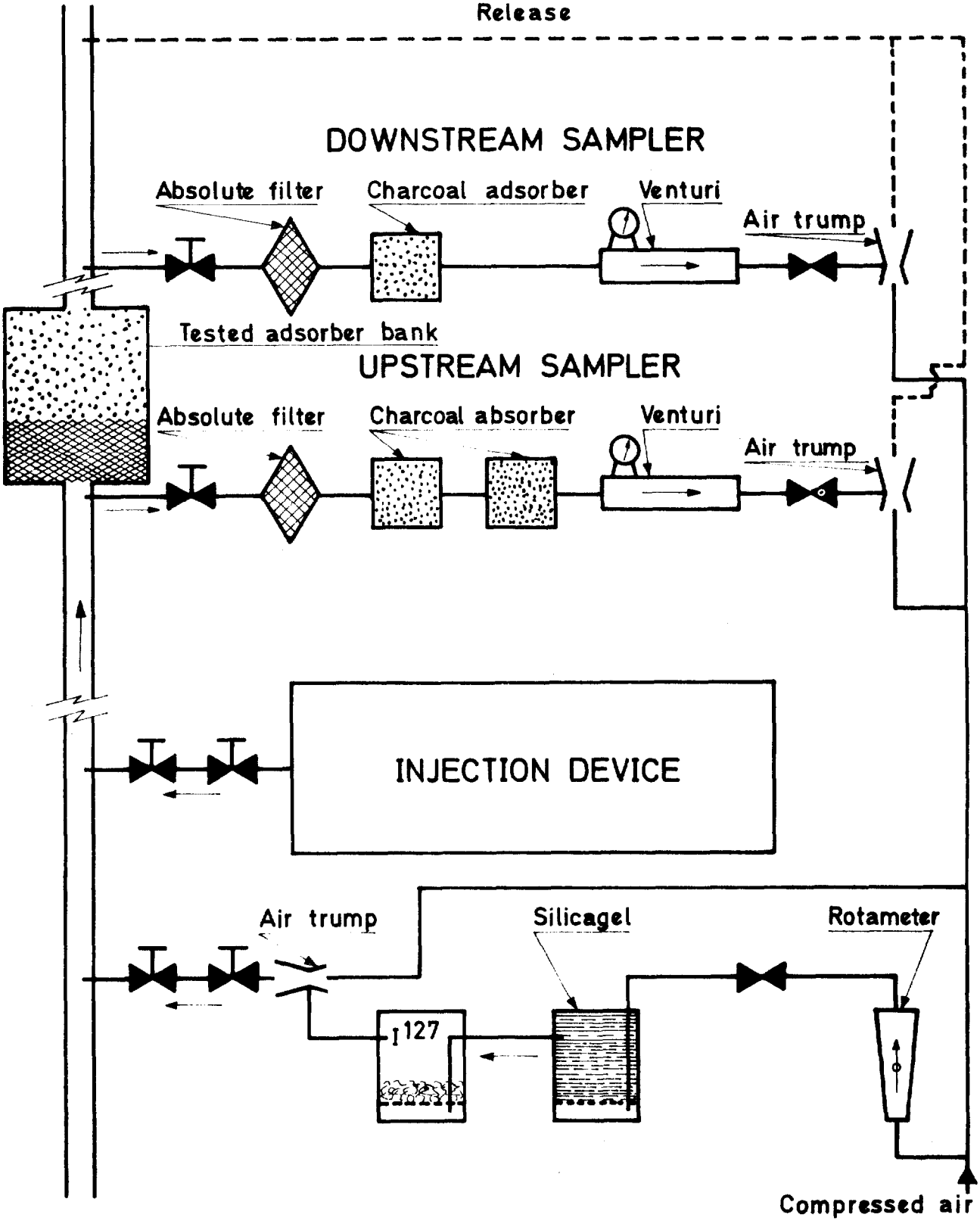

FIGURE 3 : Typical arrangement for testing an installed adsorber bank.

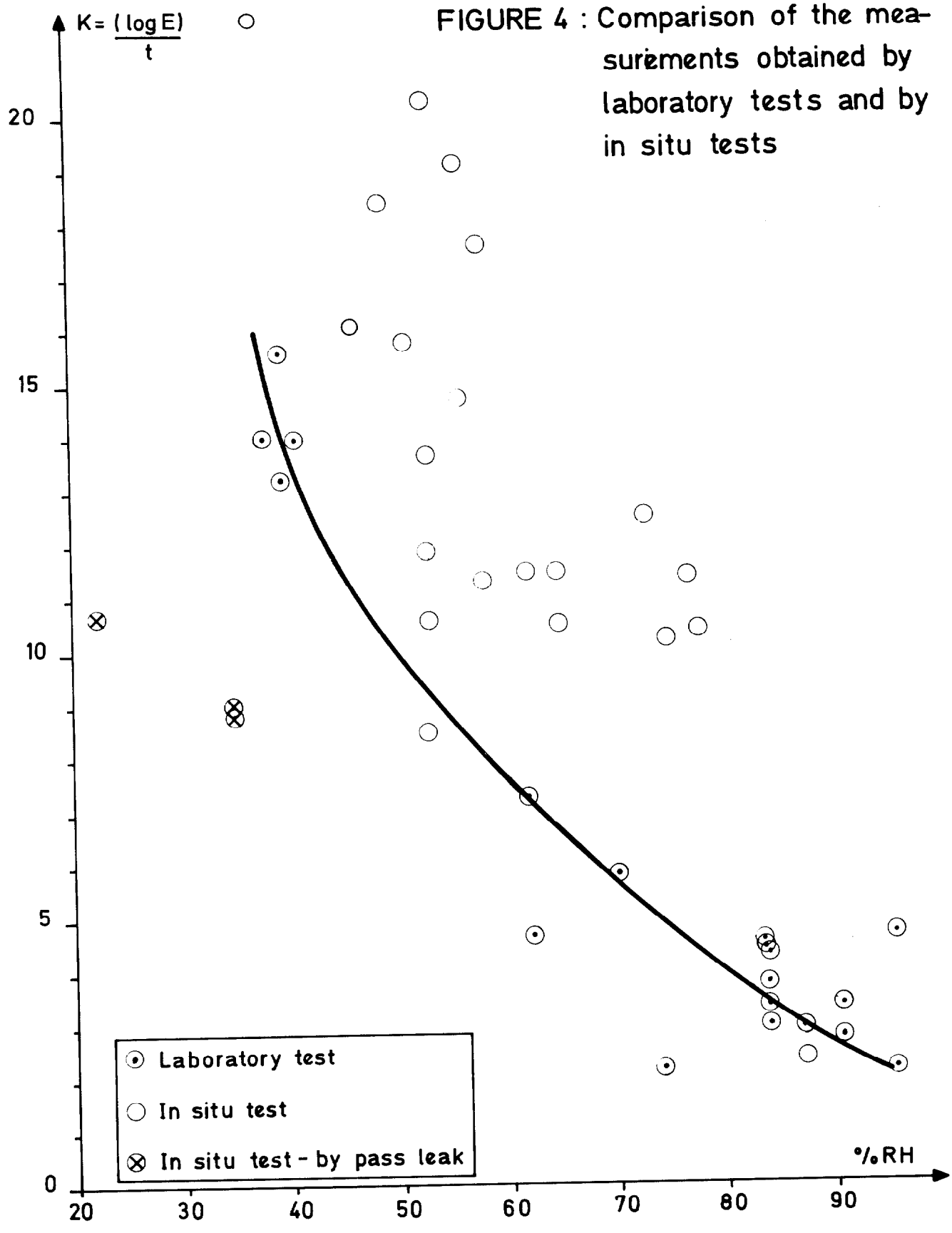

FIGURE 4 : Comparison of the measurements obtained by laboratory tests and by in situ tests

DISCUSSION

WILHELM: Did you ever try to test large charcoal units under controlled conditions and compare this with the results of the laboratory tests also under controlled conditions? I mean could you perform a kind of an in-situ test under well controlled conditions?

DECKERS: We cannot control conditions during the in-situ test, but in-situ tests have been performed over a wide range of relative humidities and at about the same residence time as during laboratory tests.

WILHELM: There is definitely a difference between your results under presumed equal conditions. We applied your method for full scale and bench scale adsorbers and we got the same results for both adsorbers. There was no scale-up factor. I think that different humidity conditions and different percentages of adsorbed water existed between the in-situ filters and the laboratory test beds.

DECKERS: In the space between primary and secondary containment, the relative humidity was very constant due to the confinement. Therefore, it was nearly equivalent to a controlled atmosphere. Due to the fact that the adsorbents were in this atmosphere, it seemed that 6 hours of operation was sufficient to obtain hygrometric equilibrium. However, it is possible that it was not the case.

HEAD-END IODINE REMOVAL FROM A REPROCESSING PLANT WITH A SOLID SORBENT

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Abstract

In the first large-scale reprocessing plant planned in the Federal Republic of Germany a total amount of 580 kg of iodine per annum will be released in the fuel dissolution process for a maximum heavy metal throughput of 1800 tons per year and 40,000 MWd/t of burnup. The main portion of the iodine is formed by the ^{129}I ($T_{1/2} = 1.6 \times 10^7$ a) isotope of which 82 Ci at the maximum are released every year. With the scheduled fuel element storage time of $\geq$ 220 d the simultaneous release of ^{131}I is $\leq$ 12.5 Ci the mass of which does not play any part.

If the off-gases were released from the dissolver in the absence of iodine removal, long-term contamination by ^{129}I of the environment would have to be expected, which would increase with continued operation.Besides, Kr separation from the off-gas, which is to be carried out in a large-scale reprocessing plant, calls for preliminary removal of the iodine.

According to the computer model presently imposed in the Federal Republic of Germany for treatment of the environmental impact by radioiodine, a total decontamination factor of 340 must be attained. This implies a long-term diffusion factor of 1×10^{-7} s/m^3 for releases via the stack of the reprocessing plant and a limit value of 50 mrem/a at the maximum for the thyroid dose to the critical group of the population via the ingestion path.

The target of current R & D work is an iodine filter attaining for safety reasons a decontamination factor higher by the factor of 10, viz. 3400. This filter is so designed that it is capable of adsorbing the total amount of iodine from the fuel. In the loaded iodine filters the iodine occurs in a solid, nearly insoluble form suitable for transportation so that no further processing steps are required.

The amount of radioiodine carried over into the process solutions of a reprocessing plant should be as low as possible. If this condition is fulfilled, filtering for iodine of the vessel off-gases and of the off-gases originating in the solidification process of radioactive waste might not be necessary. Laboratory tests as well as measurements performed in the Karlsruhe Reprocessing Plant have shown that a fraction > 99.5 % of the iodine inventory can be transferred from the fuel solution into the dissolver off-gas.

In this report the flowsheet for dissolver off-gas cleaning in a reprocessing plant employing solid iodine sorption material and the arrangement of filter components are discussed. The principle of an iodine sorption filter is described which allows exhaustive loading of the iodine sorption material. The removal reactions of different organic iodine compounds and the loading capacity and removal efficiency of the iodine sorption material in the original dissolver off-gases of reprocessing plants are indicated. Studies on the influence of filter poisons are reported.

Operating experience gathered with a first iodine sorption filter in operation is discussed; this filter has been used to remove practically all iodine produced in the dissolver off-gas of the Karlsruhe Reprocessing Pilot Plant (WAK).

Direct measurement of ^{129}I in samples of filter material using a low energy photon spectrometer is briefly reported.

I. Introduction

In the first large-scale reprocessing plant planned in the Federal Republic of Germany a total amount of 580 kg of iodine per annum will be released in the fuel dissolution process for a maximum heavy metal throughput of 1800 tons per year and 40,000 MWd/t of burnup. The main portion of the iodine is formed by the ^{129}I ($T_{1/2} = 1.6 \times 10^7$ a) isotope of which 82 Ci at the maximum are released every year. With the scheduled fuel element storage time of $\geq$ 220 d the simultaneous release of ^{131}I is $\leq$ 12.5 Ci the mass of which does not play any part.

If the off-gases were released from the dissolver in the absence of iodine removal, long-term contamination by ^{129}I of the environment would have to be expected, which would increase with continued operation.

II. Decontamination Factors Required for Iodine Removal

Since at present adequate data are not available on the dilution of radioactive iodine from the exhaust air with the inactive natural iodine occurring in the atmosphere and in the environment of the reprocessing plant, the relatively high dose ingestion factor for infants of 2×10^6 rem x m^3/Ci x s is used to calculate the thyroid dose of the critical group of population. When this value is used the calculated thyroid burden by ^{129}I largely exceeds that caused by ^{131}I (calculated on the basis of a dose ingestion factor of 4.4×10^5 rem x m^3/Ci x s and a cooling time of $\geq$ 220 d for the spent fuel) and determines to a considerable extent the requirements to the total decontamination factor for radioiodine of a plant. This value is 340 taking into account the data indicated above, a long-term diffusion factor of 1×10^{-7} s/m^3 for the iodine release via the stack, the occurrence of all the radioiodine in its elemental form, and a tolerable thyroid burden of 50 mrem/a of the critical group of population via the ingestion path.

If provisions are made for Kr removal from the dissolver off-gas, iodine must be removed with a high removal efficiency (> 99 %), independent of the previous considerations, so that the subsequent process steps for Kr removal are not interfered with.

Present R & D work concentrates on the construction of an iodine filter for a reprocessing plant of the size stated in the introduction. For safety reasons the decontamination factor of the filter will be at least 10 times higher than required by Radiation Protection Regulations for the total decontamination factor of the plant.

Therefore, the filters are to provide a decontamination factor $\geq$ 3400 and be so designed that the total iodine produced in the fuel can be removed. Taking into account the expected volume of off-gas and the wish to achieve the maximum possible loading capacity of the iodine sorption filter and to minimize the number of filter replacements, we obtain a filter design by which a much higher decontamination can be expected than required for reasons of radiation protection.

III. Removal of Aerosols - Concept of Procedure

The aerosol activity mainly originates in the shears and in the dissolver. Suitable layout of the dissolver vapor room and conduction of the sweep gas are to assure that the dust generated during fuel element cutting is separated by sedimentation in the vapor room and likewise dissolved by nitric acid.

Boiling and stirring of the fuel solution in the dissolver generates droplet aerosols whose particle diameters should be mainly above 10 μm.

On account of condensation processes and dilution in the condenser and in the NO_2 absorption and I_2 desorption columns the fuel fraction in the droplet aerosols occurring in the off-gas of individual process steps can be expected to decrease with distance to the dissolver.

The aerosol removal facilities downstream of the desorption column were selected under the following aspects:

1. Droplet aerosols must be removed as much as possible quantitatively in such a way that the liquid can be returned into the process. The fraction of aerosols removed by the HEPA - filters and consequently not eligible for recycling should be as low as possible.

2. To maintain high removal efficiencies over extended operating periods only solid aerosols should be removed by the HEPA - filters; droplet aerosols should be separated previously by appropriate devices. Droplet aerosols passing the droplet and moisture separator should have a low diameter so that they can be easily transformed into solid aerosols by heating and evaporation.

3. If possible, the iodine filter should not be exposed to radioactive aerosols so that the filter can be most conveniently handled after loading without requiring additonal shielding .

Fig. 1 shows a flowsheet of the aerosol and iodine filter arrangement which is investigated under the simulated off-gas conditions of a large-scale reprocessing plant.

Fig. 2 shows the components of head end off-gas treatment in a large reprocessing plant.

IV. Position of the Filter Train in the Flowsheet

If measurements at the test benches show that the aerosol concentration in the dissolver off-gas can be kept low, that aerosol removal safely performs also at higher NO_x-concentrations, and that the removal of droplets leads to a sufficient reduction in aerosol off-gas activity, the use of the iodine sorption filter and of the other components of the filter section, even upstream of the NO_2 absorption column for acid recovery, should be discussed (Fig. 2). By iodine removal directly from the dissolver off-gas stream before the off-gas is washed, off-gas treatment could be substantially simplified, since

1. the iodine from the recovered acid must no longer be volatilized which means that the expensive desorption step is avoided;

2. the concentration of the recovered acid might be increased by evaporation without release of residual iodine;

3. alternative methods have not to be developed to increase the concentration of the recovered acid, which would exclude an evaporation step.

The efficiency of droplet removal is decisive for the expenditure required in the subsequent stages of off-gas treatment, and therefore it must be the topic of detailed future investigations.

It was shown in laboratory tests and removal tests performed with the off-gas of reprocessing plants that the planned iodine sorption filter can be installed both upstream and downstream of the NO_2 absorption column in case that the AC 6120 iodine sorption material is used.

V. Fission Product Iodine Volatilization from the Fuel Solution

To avoid that iodine released from the fuel gets distributed in the process solutions of the reprocessing plant, the total iodine should be volatilized as completely as possible from the fuel solution already in the dissolver. This avoids and minimizes, respectively, the iodine release of the individual process steps including vitrification of high level wastes intented for ultimate storage.

For fission product iodine volatilization from the fuel solution a value of > 99 % can be assumed. Iodine, in the form of iodate, cannot be volatilized. By dissolution of UO_2 in nitric acid according to the formula

$$UO_2 + 3\ HNO_3 \longrightarrow UO_2\ (NO_3)_2 + 1/2\ NO_2 + 1/2\ NO + 1\ 1/2\ H_2O \qquad (1)$$

sufficient amounts of NO are produced to reduce iodate to elemental iodine. If necessary, NO or nitrite can be added[1].

The volatilization of elemental iodine is decisively determined by the distillation rate of the acid from the dissolver during the process of dissolution. Based on experimental work and experience gathered with the Karlsruhe Reprocessing Plant (residual iodine in the feed solution $\leq$ 0.5 %[7]) fission product iodine can be expected to be volatilized almost completely from the fuel solution. Part of the residual iodine contained in the fuel solution will be present in the vessel off-gas system. Since radiochemical reactions of tributyl phosphate, its decay products, and dodecane give rise to quite a number of organic compounds susceptible to reacting with iodine, it can be expected that in the vessel off-gas the percentage is high of organic compounds contained in total iodine release. Besides, filter pollutants occur which are an additional handicap to removal.

VI. Fission Product Iodine Removal by Solid AC 6120 Iodine Sorption Material

As an alternative to wet washing of dissolver off-gases the total fission product iodine can be directly removed by a solid sorption material. Since the off-gases contain NO_x, only inorganic iodine sorption materials such as molecular sieves and impregnated inorganic carrier materials can be used. Activated carbon is ruled out because of the risk of poisoning and ignition. Fission product iodine removal by solid sorption materials offers major advantages in cases where

1. high removal efficiencies can be achieved with the sorption material;

2. the fission product iodine is removed in a form immediately suitable for storage so that further treatment steps can be avoided;

3. the filters are designed in a simple and reliable way and can be replaced by remote handling.

The AC 6120 iodine sorption material,in a new highly impregnated version, namely AC 6120/H_1, largely satisfies the conditions enumerated above. This material is now being produced and marketed on an industrial scale. The removal of fission product iodine is due to the conversion of the $AgNO_3$ impregnation into the hardly dissolvable silver iodide and silver iodate, respectively[2,3]:

$$AgNO_3 + I_2 \longrightarrow AgI + INO_3 \quad (2)$$

$$2\ INO_3 + AgNO_3 \longrightarrow AgIO_3 + 3\ NO_2 + 1/2\ I_2 \quad (3)$$

$$INO_3 \rightleftharpoons NO_2 + 1/2\ O_2 + 1/2\ I_2 \quad (4)$$

Methyl iodide and other alkyl halides enter into reactions with the silver nitrate impregnation to become silver iodide as well, following the equation [4]

$$AgNO_3 + R\text{-}I \longrightarrow (NO_3 \cdot RI \cdot Ag) \longrightarrow RNO_3 + AgI \quad (5)$$

VII. Removal Efficiency of the AC 6120 Iodine Sorption Material

VII. 1 Laboratory Scale Tests

Comprehensive experimental data on the removal efficiency of AC 6120 have already been published[5]. Since it is intended to remove by AC 6120 the total iodine from the large reprocessing plant, the fraction of $AgNO_3$ impregnation was increased to get a higher loading capacity. The new high impregnation version AC 6120/H_1 contains 12 wt.% of Ag. Compared with the less impregnated AC 6120 this yields a slightly higher removal efficiency in the laboratory test (Tables I and II)

VII. 2 Tests Performed with the Dissolver Off-gas of SAP Marcoule

In the process of KNK fuel element dissolution, samples were taken with a sampler of the off-gas upstream and downstream of an AC 6120/H_1 test bed installed in the dissolver off-gas line.For this purpose shortly cooled EL-4 fuel was added which contained high ^{131}I fractions. To achieve high iodine loading of the test bed, $K^{127}I$ was added to the fuel solution in the dissolver. Every sampler was provided with 4 successive AC 6120 beds of 2.5 cm depth,the residence time of the off-gas in the samplers was about 0.6 s. The filter box with the test beds and the aerosol filters was coupled alternatively downstream of the dissolver and of the NO_2 absorption column of the dissolver off-gas line. In the removal tests the whole dissolver off-gas was passed over the aerosol filters and over the iodine sorption material.

In the first removal test the test beds were loaded downstream of the NO_2 absorption column over a period of 2 hours during dissolution. About 3 m^3 of off-gas (1.5 m^3/h) were passed over the filter system.

Integral measurement of the removal efficiency during sampling for the ^{131}I activity of the fission product iodine at 150°C and 35 cm bed depth yielded 99.998 % for a residence time of 1.6 s.

In the second removal test the test bed was placed upstream of the NO_2 absorption column. The filter was loaded from the beginning of HNO_3 boiling until

the process of dissolution was terminated. The sorption material already used in test No. 1 was further loaded by iodine in this removal test. 10.5 m^3 (1.5 m^3/h) of dissolver off-gas were passed over the filter section during a 7 hours period.

Integral measurement of the removal efficiency at 150°C and with the bed depth and residence time indicated above yielded 99.9992 %. This value was also measured via the ^{131}I activity removed by the upstream and downstream samplers.

The difference in penetration, 2×10^{-3} as compared to 8×10^{-4} %, is within the experimental accuracy and does not allow to draw conclusions as to the differences in removal efficiencies of the AC 6120/H_1 test bed as a function of preconditioning of the dissolver off-gas.

The results of these and other removal tests have been presented in Table III. Fig. 3 shows the removal profiles of the upstream samplers for the tests Nos.2, 7, 5,and 6.

Fig. 4 shows a test rig installed at WAK, which allows to continue the investigations of iodine sorption materials.A set-up similar to this test rig was used for the investigations at SAP Marcoule.

VII. 3 Operating Behavior of an Iodine Sorption Filter Used to Clean the WAK Dissolver Off-gases

Complying with requirements by the authorities an iodine sorption filter made up of AC 6120 was installed at WAK in September 1975 which provides for cleaning of the dissolver off-gas during operation. Fig. 5 shows a flowsheet of the WAK off-gas cleaning system and of the sampling points for control of the iodine sorption filter. The filter bed consisted of 26 kg of low impregnation AC 6120 (7 % Ag) since at that time sufficient amounts of the high impregnation AC 6120/H_1 material were not available. For an average volumetric flow of 148 m^3/h of the dissolver off-gas the residence time was 1.0 ± 0.4 s at an operating temperature of 130°C. The NO_x concentration in the off-gas was < 2 vol. %; this value has been averaged over the whole period of dissolution. Short-term concentration peaks up to 20 vol.% of nitric oxides must be assumed. During the use of the iodine sorption filter LWR fuel was processed which had an average burnup of 25.000 MWd/t of uranium. More than 99.5 % of the fission product iodine contained in the fuel were transferred into the dissolver off-gas. At the end of dissolution only fractions < 0.5 % of the theoretical ^{129}I content of the fuel (calculated with the ORIGEN code (6)) were found in the feed solution(7).

The washing solution in the washer preceding the iodine sorption filter was from neutral up to 3 M of nitric acid and attained a removal efficiency of about 1 % for ^{129}I. The washing solution was returned by batches into the dissolver.

The decontamination factor of the iodine sorption filter was determined from the ratio of ^{129}I concentrations in the upstream and downstream gas and ranged from $1.0 \pm 0.4 \times 10^4$ to $2.0 \pm 0.5 \times 10^4$ over the whole 120 days of service life of the iodine filter.At the end of filter operation a fission product iodine mixture was removed with 172 mCi ^{129}I corresponding to a total iodine amount of about 1.3 kg I_2. This is equivalent to about 60 % of the capacity of the iodine sorption filter.

Fig. 6 shows the removal profiles of upstream and downstream samplers used to monitor the iodine sorption filter installed in WAK. The ^{129}I activity was plotted over the number of successive individual beds. The samplers were provided with 8 successive 2.5 cm deep filter beds made of AC 6120 and exposed to a 220 l/h partial flow at 110 ± 10°C. The residence time of the dissolver off-gas in a

sampler was about 1.6 s. Two different iodine compounds can be clearly distinguished in the removal profile of the upstream sampler represented in Fig. 6. They are retained with considerably differing removal efficiencies. In the filtered gas only the component is found which is more difficult to remove. At the time of sampling (Fig. 6) the iodine sorption filter had taken up about 70 mCi of ^{129}I corresponding to 24 % of the theoretical capacity. During the period of exposure of the sampler shown in the figure 420 kg of fuel with a theoretical ^{129}I content (according to the ORIGEN code) of 12 mCi had been dissolved.

Complying with a requirement of the licensing authority the iodine sorption filter was monitored without interruption over the whole period of operation and the samplers were replaced after dissolution of 3 to 5 fuel batches each containing 140 kg of fuel. After about 60 % of the silver in the iodine sorption filter had reacted with the fission product iodine, the filter was withdrawn according to the requirements. The surface dose rate of the filter was 80 mrem/h at the end of its service life.

So, the iodine sorption filter was dismounted after 120 days of use. AC 6120 had an excellent flow capacity and showed but slight yellow and grey shading.

All the ^{129}I determinations for the WAK iodine sorption filter were made by direct measurement with a Low Energy Photon Spectrometer (LEPS) after the accuracy and usefulness of the method had been proved by comparison with the results obtained with activation analysis. The agreement of measured values with the ^{129}I yields calculated using the ORIGEN code with a tolerance limit of 10 % can be considered as the experimental validation of the measurement technique.

VIII. Silver Consumption and Loading Capacity of Iodine Sorption Filters Made of AC 6120/H_1

The consumption of silver is a decisive cost factor of the removal method described. It is attempted to achieve as much as possible a quantitative reaction of silver. According to the reaction equations (2) to (5) on page 5, 143 g of ^{129}I can be removed by 1 kg of AC 6120/H_1 when $AgNO_3$ reacts by 100 % with iodine.

Laboratory studies have shown that 75 - 94 % of silver in the impregnation react with iodine (see Tables IV to VII). Fig. 7 shows a removal profile obtained in the laboratory test for loading an AC 6120/H_1 filter bed with radioactively marked I_2 up to 58 % of its capacity, whose bed depth is the same as that planned for a large reprocessing plant. The plot shows the amount of iodine removed by each bed section and the penetration dependent on the bed depth and on the loading. The filter beds loaded with I_2 in the laboratory tests usually achieved a decontamination factor of the order of 10^4 up to some 60 % utilization of the loading capacity(measured for the total period of loading).

The iodine sorption filter used for cleaning during operation of the dissolver off-gases from WAK yielded a decontamination factor of 10^4 after 60 % of the total silver had reacted with fission product iodine. This indicates that also in practical filter operation the reacted amount can be high.

With silver molecular sieves, type Linde 13 X Ag, a lower utilization of silver was measured in the laboratory under identical conditions. The reacted amount (Tables VIII and IX) ranged from 35 % (5 % NO_2, 150°C) to 56,4 % (0 % NO_2, 150°C). A comparison of the silver utilisation as a function of bed depth for the iodine sorption materials AC 6120/H_1 and MS 13 X Ag is also given in Fig. 15.

IX. Reaction of AC 6120 Iodine Sorption Material with Organic Iodine Compounds

Since in the off-gases of a reprocessing plant, in particular in the vessel off-gas, the presence of organic iodine compounds must be anticipated, the reaction behavior with respect to AC 6120 was investigated for a number of organic iodine compounds. Detailed investigations were made of the reactions of straight chain alkyl iodides $C_n H_{2n+1}I$ (n = 1-12), secondary and tertiary alkyl iodides (model substance: secondary and tertiary butyl iodide), alicyclic iodine compounds (model substance: iodine cyclohexane), side-chain substituted aromatic cyclic compounds (model substance: benzyl iodide) and ring substituded aromatic iodide compounds (model substance: iodobenzene) with AC 6120 under cover gas atmosphere. The reaction products were trapped in cooling traps and separated by gas chromatography. They were identified by determination of the retention time and, if necessary, by IR-spectrometric analysis in addition[8].

Figs. 8 and 9 show some of the gas chromatograms of the model substances and their reaction products following the reaction in a 2.5 cm deep AC 6120 bed and with a residence time of 0.1 s. The reaction temperature was 150°C in the tests shown in Fig. 9. The iodine compounds and reaction products are given in Tab. X.

According to these tests on the removal of organic iodine compounds difficulties should not be encountered in iodine sorption with the inorganic AC 6120 sorption material in the off-gases of a reprocessing plant.

The primary alkyl iodides react with AC 6120 to become AgI and alkyl nitrates and into alkanes with a lower yield. The secondary alkyl iodides form AgI, alkenes and HNO_3 when they react with AC 6120. The tertiary alkyl iodides convert into AgI, alkenes and HNO_3.

As for the primary alkyl iodides the reaction rate of the secondary and tertiary alkyl iodides decreases with the chain length. Tertiary alkyl iodides react much faster with AC 6120 than primary and secondary alkyl iodides.

Iodocyclohexane reacts with the $AgNO_3$ impregnation like a straight chain secondary alkyl iodide while forming AgI and cyclohexene. Like the primary alkyl iodides benzyl iodide reacts with $AgNO_3$ to become AgI and benzyl nitrate. Also at temperatures up to 180°C iodobenzene does not react with the $AgNO_3$ impregnation of AC 6120.

With respect to the German fuel reprocessing plant, it is not planned to use aromatic compounds in the extraction procedure. So it is not expected that aryl halides will occur in the exhaust air in quantities which would substantially impair the filter efficiency.

In case that the previous dissolution and extraction steps will be modified, aromatic substances, which are susceptible to iodination, should not be used.

X. Influence of Filter Pollutants on the AC 6120 Iodine Sorption Material

X. 1 Behavior of AC 6120 with Respect to Dodecane and Tri-n-butyl Phosphate

When recycled acid is used the dissolver off-gases might contain small amounts of dodecane employed as the solvent and of tributyl phosphate and its decay products used as an extractant in the PUREX process.

In the vessel off-gas higher fractions of these organic pollutants must be expected; dodecane and radiolytic products of tributyl phosphate were detected. The reactions in air between AC 6120 and dodecane and tributyl phosphate, respectively,were investigated at the operating temperature provided for the iodine sorption filter.

The concentration was 1.9×10^{-2} g dodecane/l air and 6.1×10^{-3} g tributyl phosphate/l air while the residence time of the gas mixture in the iodine sorption bed was 0.4 s and the linear air velocity was 25 cm/s. The reaction products were detected by gas chromatographic analysis.

Dodecane was completely inert with respect to AC 6120. Tributyl phosphate was converted into a silver phosphate of not clarified structure. Butyl nitrate at low concentrations (< 5 % related to the total tributyl phosphate inventory) was determined by gas chromatography as a gaseous reaction product.

While AC 6120 in the NO_x carrying off-gas from the dissolver normally yielded but slight discoloration and no major reduction in removal efficiency as a result of the reaction with pollutants,AC 6120 used in the vessel off-gas underwent a very intensive grey-blue discoloration which was accompanied by a substantial reduction in removal efficiency and is attributable to a conversion of $AgNO_3$ of the impregnation resulting in Ag_2O. Part of the organic impurities in the vessel exhaust air acted as a reductant with respect to $AgNO_3$ of the impregnation.

X. 2 Regeneration of the AC 6120 Iodine Sorption Material after Poisoning in the Vessel Off-gas

It was observed that the discoloration resulting from vessel off-gas was eliminated by an NO_2-air mixture flow and that at the same time the removal efficiency could be largely restored.

Fig. 10 shows the results of three laboratory tests (plots 1, 2 and 3) with AC 6120 previously exposed over 20 days to the vessel off-gas from a reprocessing plant.

Plot 1 shows the penetration of the poisoned AC 6120 test beds by $CH_3{}^{131}I$ in air (temperature 150°C, dew point 30°C, linear air velocity 25 cm/s). The penetration is very high with respect to fresh AC 6120 (plot 4). Plot 2 shows the penetration of AC 6120 after a regeneration period of 24 hours in a mixture of air and 2.5 % NO_2. During exposure to methyl iodide the carrier gas was also NO_2 containing air. The other conditions are the same as indicated above.

Plot 3 shows the penetration of AC 6120 after a regeneration period of 21 h in air with 2.5 % NO_2; however, the apparatus and the adsorber material were flushed by NO_2-free air over several hours. During exposure to methyl iodide only air (no NO_2 added) was used as the carrier gas in order to avoid the influence of NO_2 on the methyl iodide used as the test medium (other conditions as above).

Fig. 11 shows the results of two removal tests performed in the laboratory with AC 6120 previously exposed to dissolver off-gas over 20 days.

The conditions of the laboratory tests (the results of which have been represented by plots 1 and 2 in Fig. 11) correspond to that indicated for plots 1 and 2 of Fig. 10. Since the dissolver off-gas contains NO_2 and organic impurities of the gas stream are negligible only, poisoning as in the vessel off-gases is not expected. Accordingly, no regeneration effect can be observed in the removal

test performed in the laboratory when NO_2-bearing carrier gas is used.

The following conclusions can be drawn from the plots:

- AC 6120 is poisoned in the vessel off-gases in addition to iodine loading. By the action of NO_2 the effect of poisoning is largely cancelled (comparison of plots 1 and 3, Fig. 10).

- By a low NO_2 content in the off-gases to be filtered AC 6120 poisoning can be largely avoided. Lower penetration and longer service lives of the iodine filter can be expected as a result.

- Since NO_2 appears in the dissolver off-gases of a reprocessing plant, the off-gases from the vessel and from the dissolver could be mixed upstream of the iodine filter. However, this should be done only in case that the amounts of iodine in the vessel off-gases are so high that they must be removed and that by admixture of the vessel off-gases upstream of the filter the removal efficiency is not markedly reduced for the relatively high iodine amounts from the dissolver off-gases. If the iodine released from the fuel is to be removed as completely as possible with the help of the iodine sorption material (off-gas cleaning without iodine washer) separate iodine filtering is recommended for the dissolver and the vessel off-gases. Also the admixture of the NO_2-bearing dissolver off-gases, already cleaned in an iodine sorption filter, to the vessel off-gas upstream of the iodine sorption filter installed for the vessel off-gas is recommended.

X. 3 Influence of NO_2 and NO on the Removal Efficiency of Fresh AC 6120

The operating temperature provided for the iodine sorption filter is 150°C. This excludes condensation of nitric acid and a higher adsorption of nitric oxides on the iodine sorption material.

According to the reaction equation indicated above (4) it can be expected that the removal efficiency decreases with increasing NO_2 concentration. In high loading tests with I_2 and air as the carrier gas no systematic influence of NO_2 concentration on the removal efficiency was observed in the range under investigation up to 5 % of NO_2 (cf. Tables IV to VII).

In a test series investigating the influence of NO_2 concentration on $CH_3{}^{131}I$ removal an increase in penetration from 0.0004 to 0.003 % of a 10 cm deep test bed made of AC 6120 was found for an increase from 1 to 10 % in the NO_2 content of the carrier gas (air) [5].

Since the carrier gas in the off-gas section of the dissolver might be nitrogen in case of subsequent Kr removal by cryogenic distillation, the behavior of AC 6120/H_1 in N_2/NO_x mixtures was investigated in some laboratory tests. NO in pure nitrogen reduces to metallic silver the $AgNO_3$ impregnation of AC 6120/H_1. This results in a loss of removal efficiency. This reaction can be suppressed by the presence of NO_2.

XI. Design of Iodine Filters for a Large Reprocessing Plant

XI. 1 Layout

Fig. 1 is a flowsheet with the planned filter sections for a large reprocessing plant. The filter containing the AC 6120/H_1 iodine sorption material will be so designed that silver in the sorption material reacts as quantitatively

as possible with iodine. The number of filter stages required is determined by the iodine concentration gradient in the sorption material and by the necessity to use as completely as possible the sorption material to be discarded. The concentration gradient achievable is depending on the volumetric flow and the linear gas velocity, respectively. It is intended to use a 2-stage iodine filter whose first filter drum in the direction of flow is loaded by iodine until it becomes exhausted, while the second filter drum is loaded to a little extent only until breakthrough of the first drum occurs. After the filter drum loaded up to exhaustion has been withdrawn, the partially loaded filter drum is transferred into the first position in the direction of flow and loaded until exhaustion.

As an alternative a method is investigated which relies on fixed filter positions. A discontinuous migrating bed filter will be developed in case that the good ability to flow of the iodine sorption material at AC 6120/H_1 filters should be confirmed.

XI. 2 Requirement of Storage Space

If 100 % of throughput is attained in a large reprocessing plant, a filter must be replaced every 6 days. The filter elements directly fit into the iron-hooped drums used for radioactive waste. About 50 iron-hooped drums of 200 l capacity will be filled every year. This means that only little storage space is required. The behavior of iodine loaded AC 6120/H_1 in salt will be the subject of further investigations. In case that the requirements of leachability of fission product iodine will not be met in the ultimate storage facility, it is planned to cement into 400 l drums the 200 l iron-hooped drums containing AC 6120/H_1.

References:

(1) E. Henrich et al., Jodbehandlung bei der Brennstoffauflösung,Reaktortagung 1976, Proceedings.

(2) W.C. Schmidt, Treatment of Gaseous Effluents, TID-7534, p. 371 (1957).

(3) K.C. Patil et al., The Silver Nitrate-Iodine Reaction: Iodine Nitrate as the Intermediate, J. Inorg. Nucl. Chem. 29, p. 407 (1967).

(4) J.G. Wilhelm, H.G. Dillmann, K. Gerlach, H. Schüttelkopf, KFK 1565, p. 175 (1971).

(5) J.G. Wilhelm, H. Schüttelkopf, An Inorganic Adsorber Material for Off-Gas Cleaning in Fuel Reprocessing Plants, CONF-720 823, p. 540 (1972).

(6) M.J. Bell, ORNL Isotope Generation and Depletion Code, ORNL 4626 (1974).

(7) Privat communication, H. Schüttelkopf, GfK.

(8) J. Furrer, R. Kaempffer, Untersuchung der Reaktionen von organischen Jodverbindungen mit feinst auf amorpher Kieselsäure verteiltem Silbernitrat, Mh. Chem. Bd. 107/IV, p. 933-938 (1976).

Annex: Direct Measurement of ^{129}I with the Low Energy Photon Spectrometer

In the measurements performed to determine the decontamination factor of the WAK iodine sorption filter iodine-129 on the iodine samplers is measured in a non-destructive way by use of a Low Energy Photon Spectrometer (LEPS). After careful mixing of the filter material two 1 g samples each were taken from each filter bed, weighed into small glass flasks and analyzed. The mean value of the two single measurements was converted to the total bed weight and the result attributed to the respective filter bed. The direct measurement of ^{129}I in the filter material samples using LEPS is briefly described below.

Iodine-129 decays via β-decay with a maximum β-energy of 150 keV into an excited instable state of ^{129}Xe (Fig. 12). $T_{1/2}$ of ^{129}I is 1.6×10^7 a resulting in a correspondingly low specific activity of 0.176 mCi/g. The excited ^{129}Xe nucleus ($T_{1/2} = 10^{-9}$ s) deactivates into the stable ground state either spontaneously while emitting a 39.6 keV γ-quantum with an absolute intensity of 7.5 % or by internal conversion. As a result of internal conversion the ^{129}-Xe atom emits its characteristic X-rays whose energies and absolute intensities related to ^{129}I decay are represented in Fig. 12 together with the data on γ-radiation.

For direct ^{129}I detection all the five lines traced in Fig. 12 are appropriate. It should be noted in this context that the X-ray lines are not only specific to ^{129}Xe and hence to ^{129}I but that they can be generated also by other active iodine isotopes with mass numbers greater than 127 by β-decay into Xe and subsequent stabilization by internal conversion (e.g. ^{131}I).

For application in reprocessing of irradiated fuels this fact, however, does not imply a limitation since any interfering iodine isotopes are short-lived and also their parents are not long-lived. The only exception is iodine-131 with a half-life of 8 days, which must be taken into account for extremely short cooling periods (< 180 days).

If disturbing ^{131}I amounts must be expected, it is recommended to make the detection by means of the 39.6 keV γ-line which is specific to ^{129}Xe and hence to ^{129}I.

However, it appears from Fig. 12 that detection by the two intensive X-ray lines ($K\alpha_1$ and $K\alpha_2$) is about 8 times more sensitive than detection by the γ-line since the two X-ray lines are measured together and thus yield a 57 % decay probability as against 7.5 % of the γ-line.

To satisfy the special requirements of ^{129}I analysis in reprocessing irradiated nuclear fuels, the following conditions should be fulfilled by the detector:

1. Very high response for γ-quanta with energies between 20 and 40 keV.

2. Very high sensitive area.

3. Resolution better than 500 eV.

4. The response of the detector should be negligible for quanta with energies above 100 keV so that the disturbing background by Compton scattering of higher energetic γ-quanta can be kept low.

For this reason Low Energy Photon Spectrometers with planar horizontal Ge(Li) detectors were used, with the following characteristics:

Sensitive area	500 mm^2
Sensitive depth	7 mm
Window	0.5 mm Al
Resolution	< 0.5 keV at 60 keV
Response at 30 keV	$\sim$ 100 %

For the absolute calibration of detectors an NBS ^{129}I standard solution (SRM 4949) was used as a primary standard (Fig. 13). The ^{129}I loaded AC 6120 was calibrated against the NBS standard indicated above by means of activation analysis. The calibration curves are linear from the experimental detection limit at $\sim 2 \times 10^{-12}$ up to more than 10^{-7} Ci ^{129}I per ml or g AC 6120, both for measurements at the 39.6 keV-γ-line and for the more intensive sum peak of the $K\alpha_1$ and $K\alpha_2$ X-ray lines of ^{129}Xe.

Fig. 14 shows the spectrum of an AC 6120 sample loaded with 6.3×10^{-7} Ci ^{129}I in the WAK dissolver off-gas.

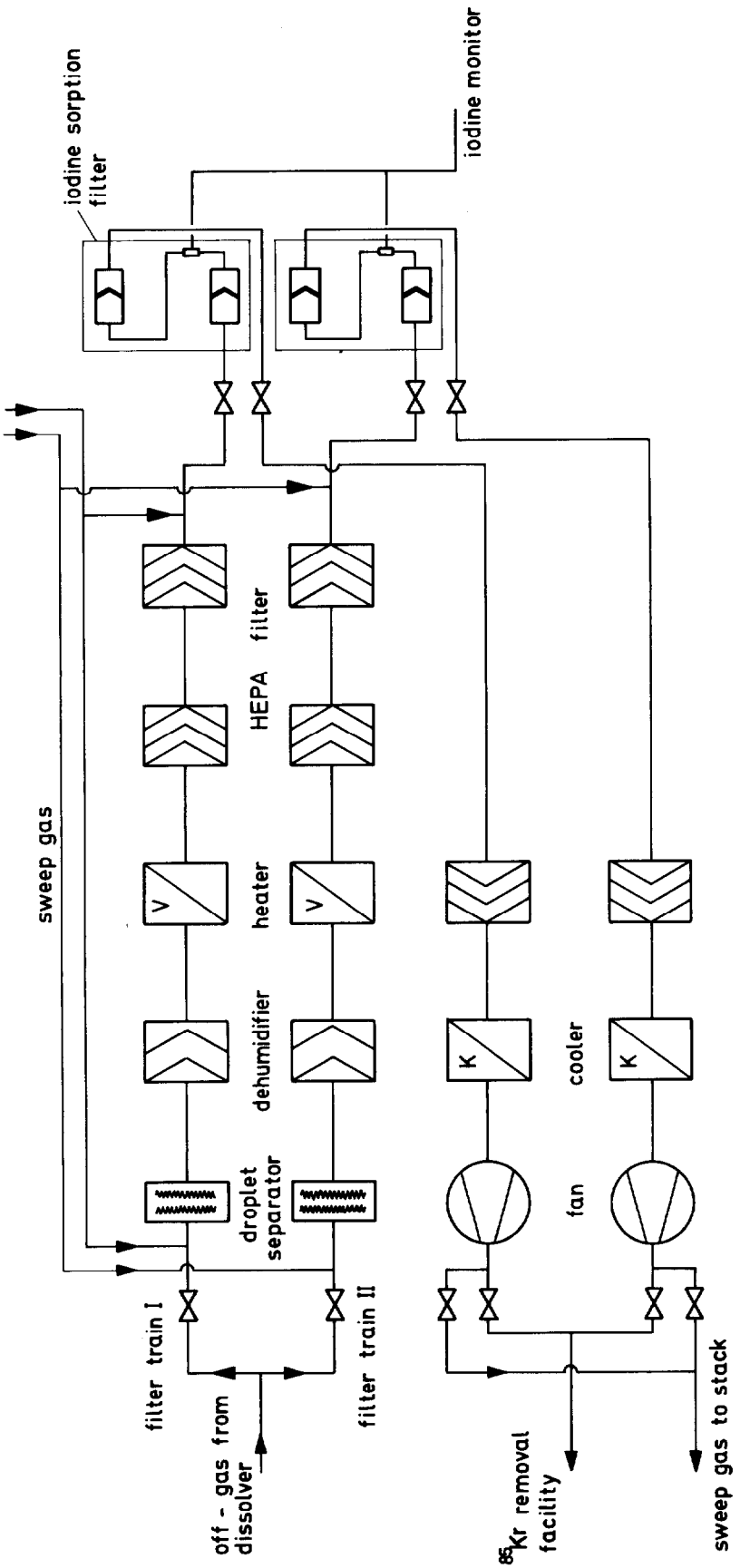


FIG. 1 Filter train for a large reprocessing plant

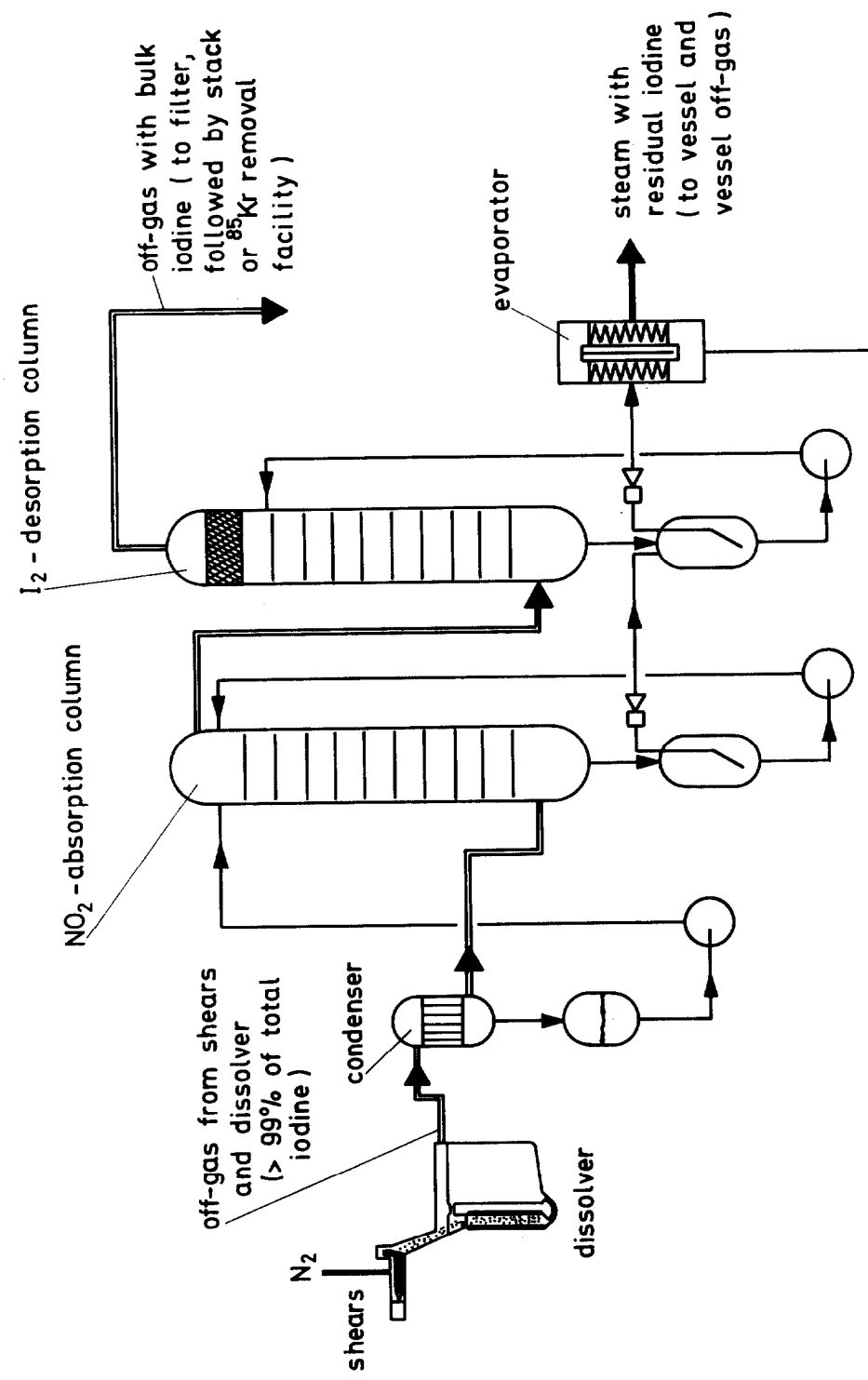


FIG. 2 Path of the fission product iodine in the head end of a reprocessing plant

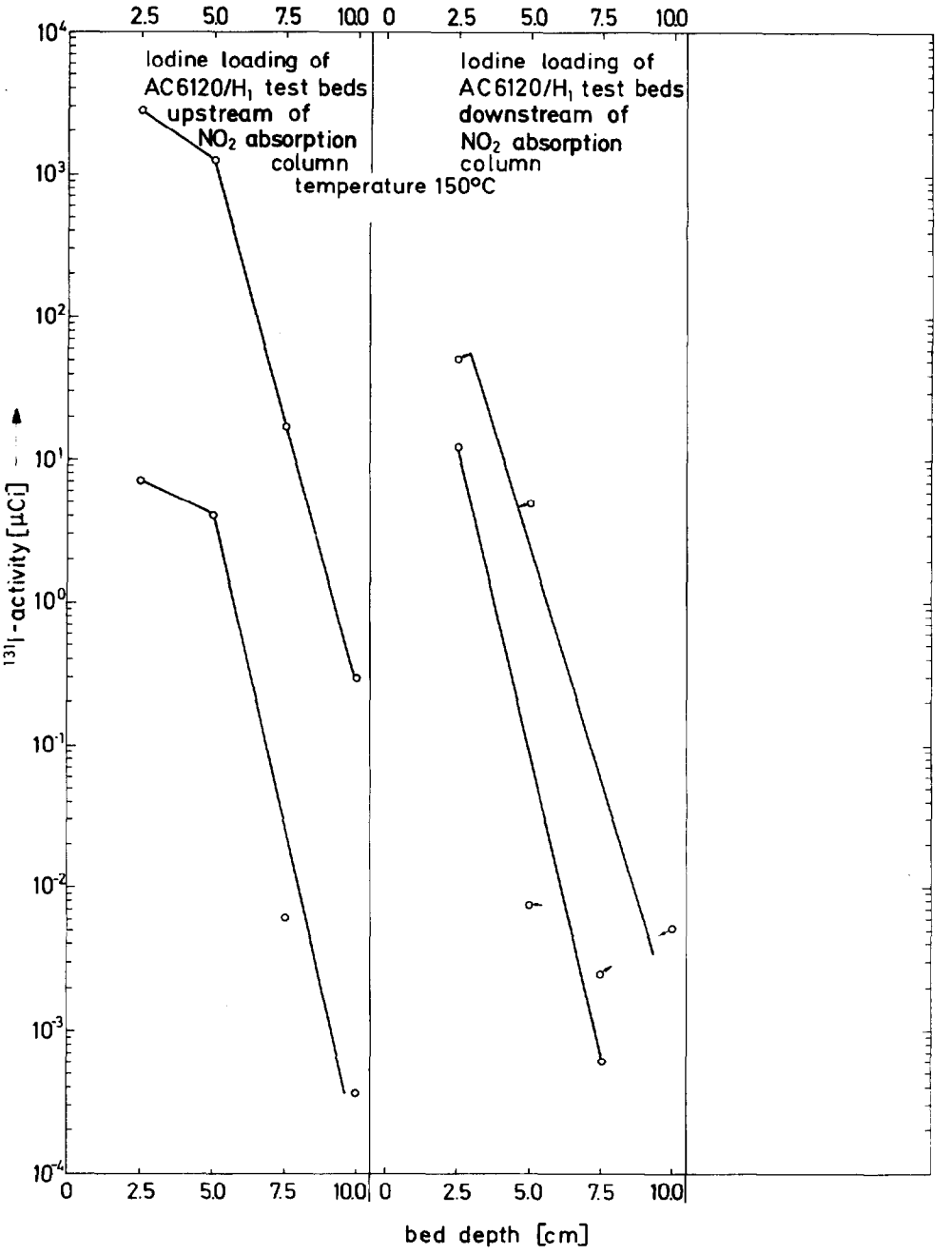


FIG. 3 Iodine removal from dissolver off-gas by AC 6120/H_1

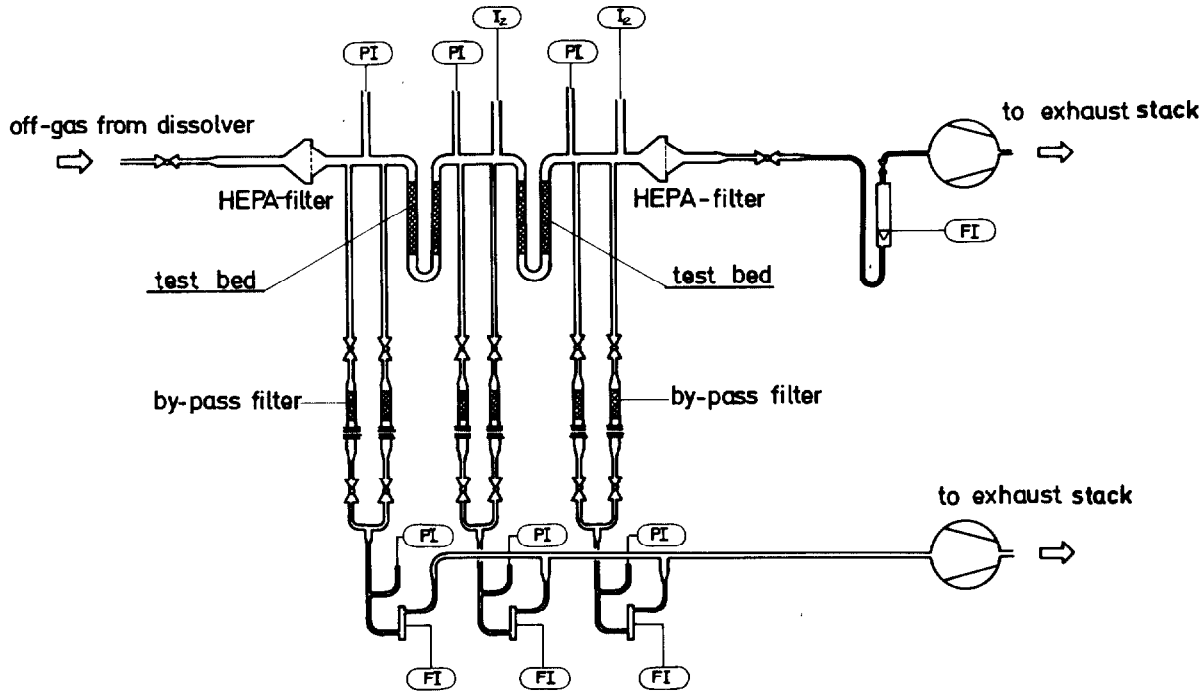


FIG. 4 Test rig for iodine sorption material in the dissolver off-gas of the Karlsruhe Reprocessing Plant (WAK).

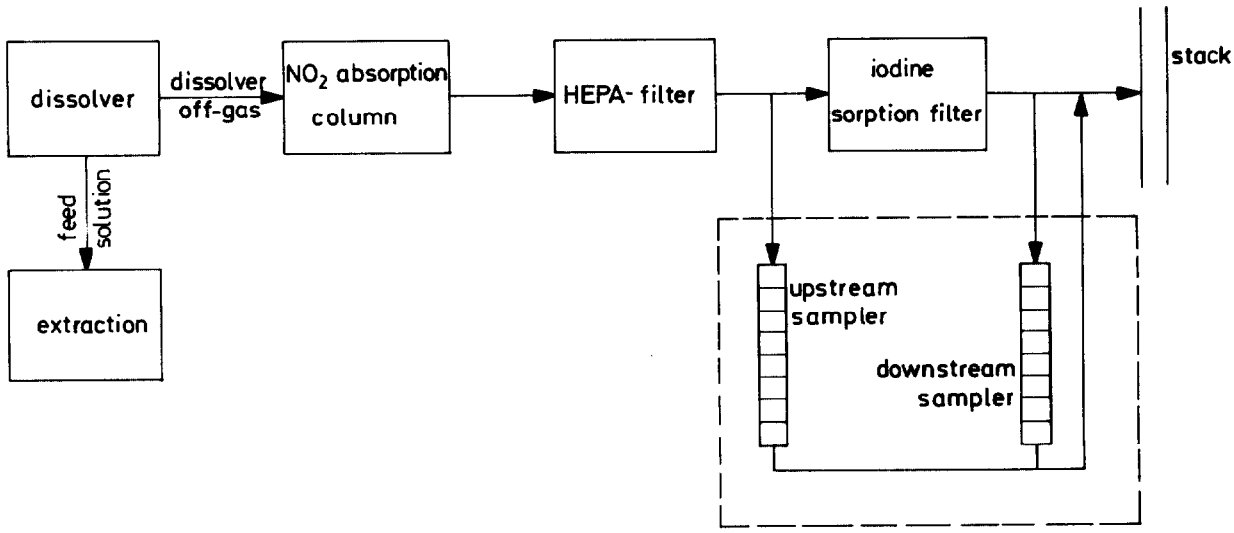


FIG. 5 Flow sheet of the WAK dissolver off-gas system

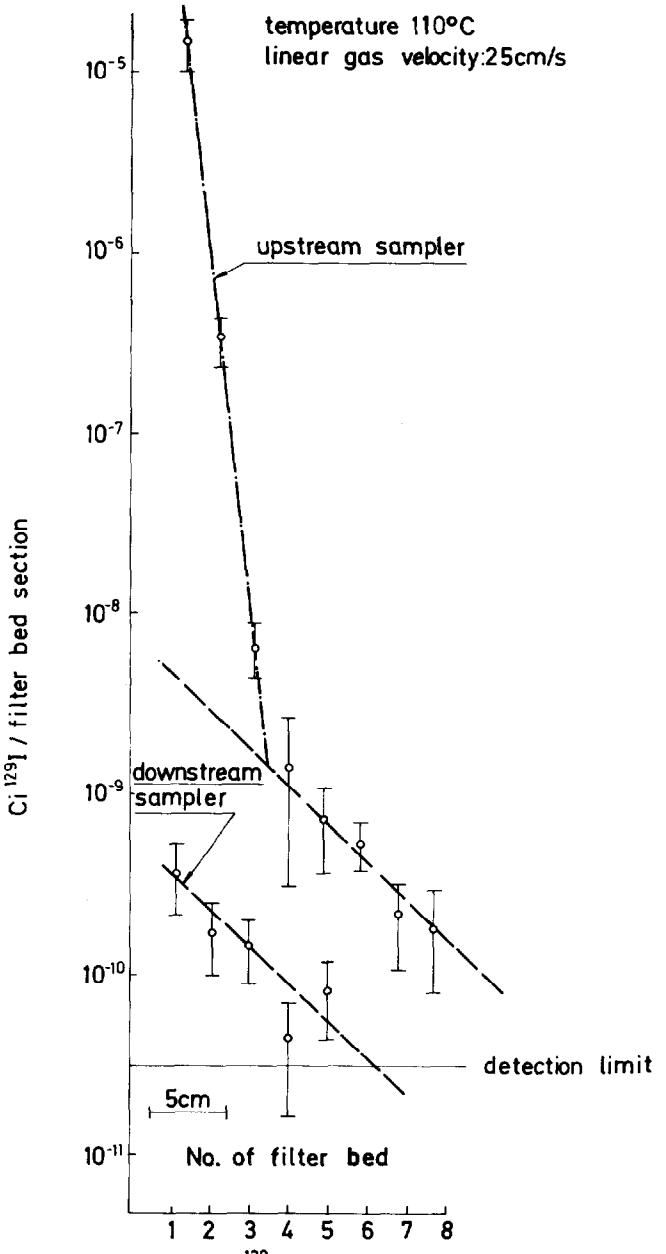


FIG. 6 Activity profile of ^{129}I in AC 6120 samplers upstream and downstream of the dissolver off-gas filter of WAK

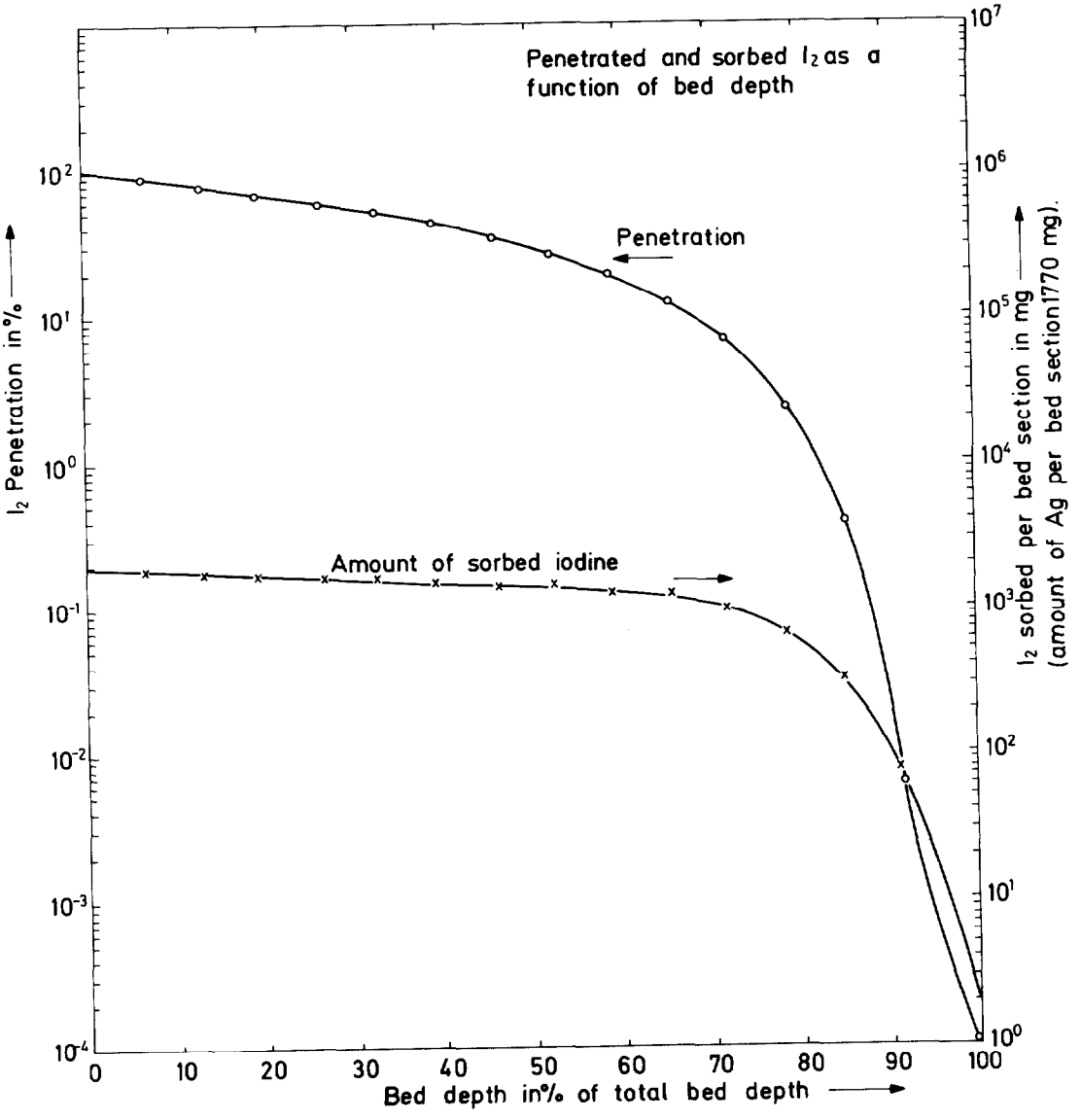


FIG. 7 Loading of AC 6120/H_1 test beds with large amounts of I_2

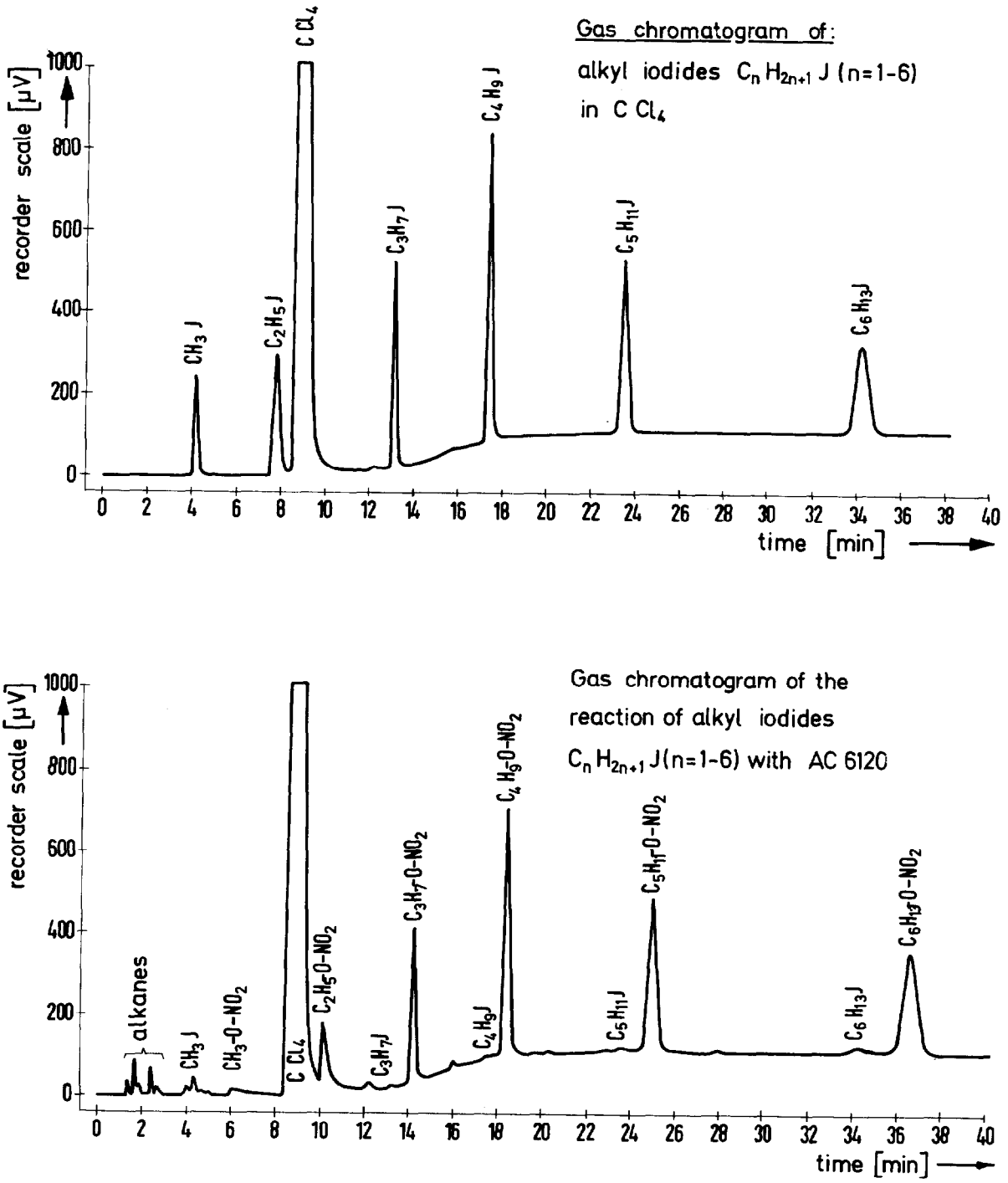
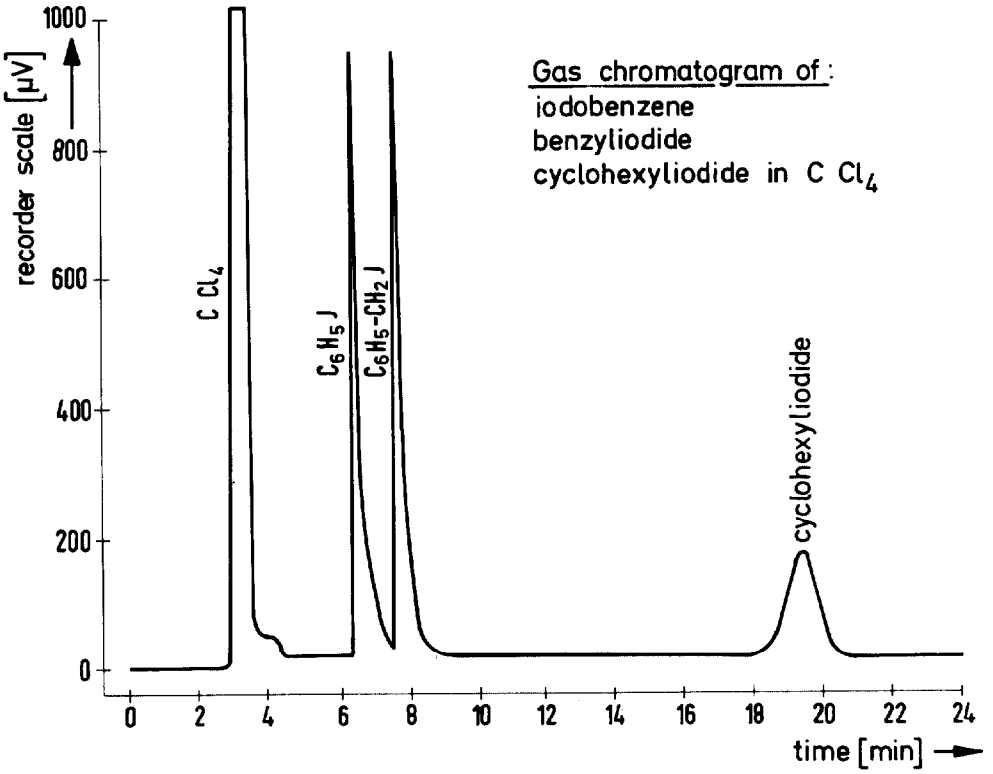

Gas chromatogram of:
alkyl iodides $C_n H_{2n+1} J$ (n=1-6)
in $C Cl_4$
recorder scale [µV]
time [min]
$CH_3 J$
$C_2H_5 J$
$C Cl_4$
$C_3H_7 J$
$C_4H_9 J$
$C_5H_{11} J$
$C_6H_{13} J$
Gas chromatogram of the
reaction of alkyl iodides
$C_n H_{2n+1} J$(n=1-6) with AC 6120
alkanes
CH_3-O-NO_2
$C_2H_5-O-NO_2$
$C_3H_7-O-NO_2$
$C_4H_9-O-NO_2$
$C_5H_{11}-O-NO_2$
$C_6H_{13}-O-NO_2$

FIG. 8


recorder scale [µV]
1000
800
600
400
200
0
C Cl4
C6H5J
C6H5-CH2J
cyclohexyliodide
0 2 4 6 8 10 12 14 16 18 20 22 24
time [min]
Gas chromatogram of:
iodobenzene
benzyliodide
cyclohexyliodide in C Cl4

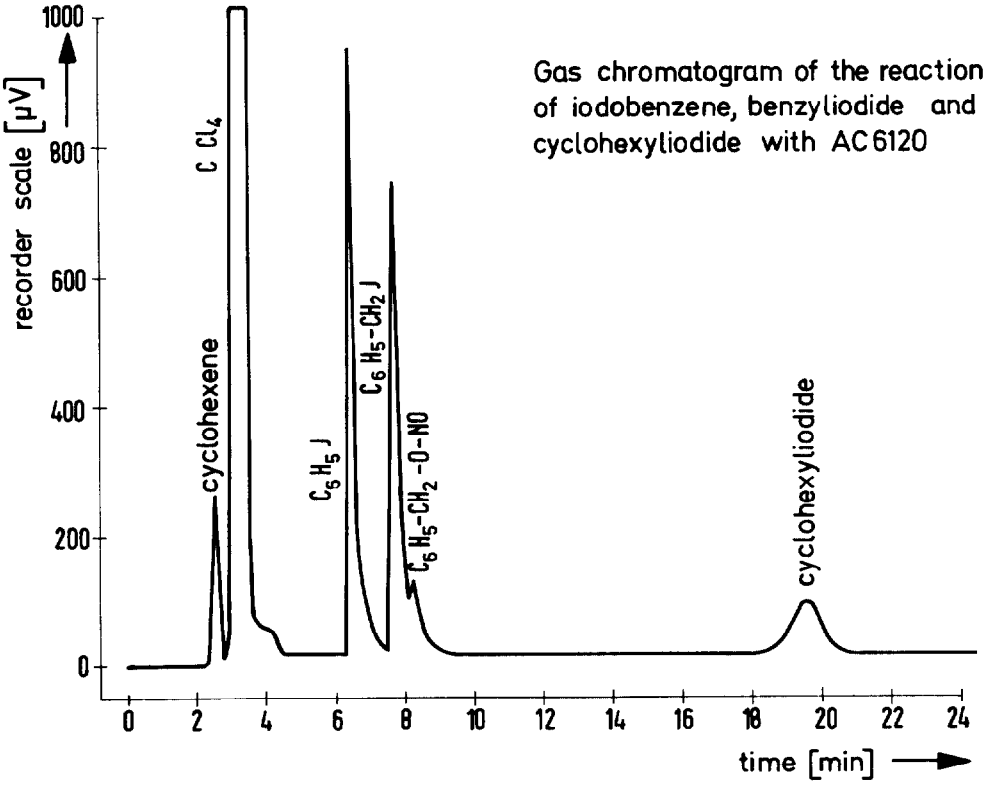

recorder scale [µV]
1000
800
600
400
200
0
C Cl4
cyclohexene
C6H5J
C6H5-CH2J
C6H5-CH2-O-NO
cyclohexyliodide
0 2 4 6 8 10 12 14 16 18 20 22 24
time [min]
Gas chromatogram of the reaction of iodobenzene, benzyliodide and cyclohexyliodide with AC6120

FIG. 9

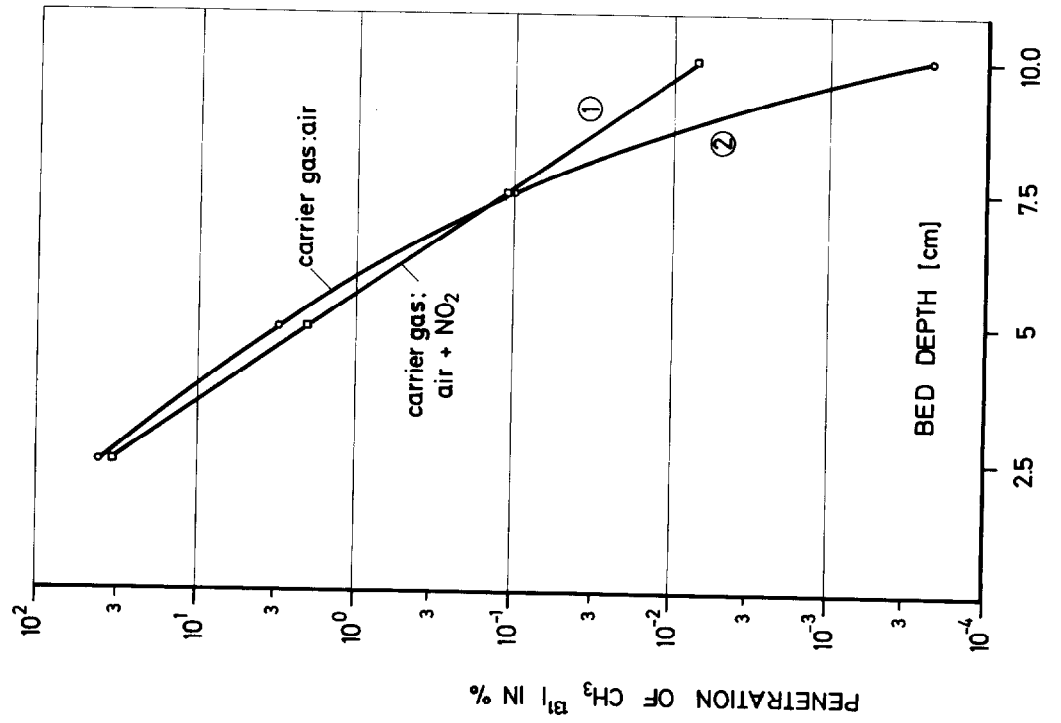


FIG. 11 Penetration of AC 6120 test beds by CH_3 ^{131}I after use in dissolver off gas.

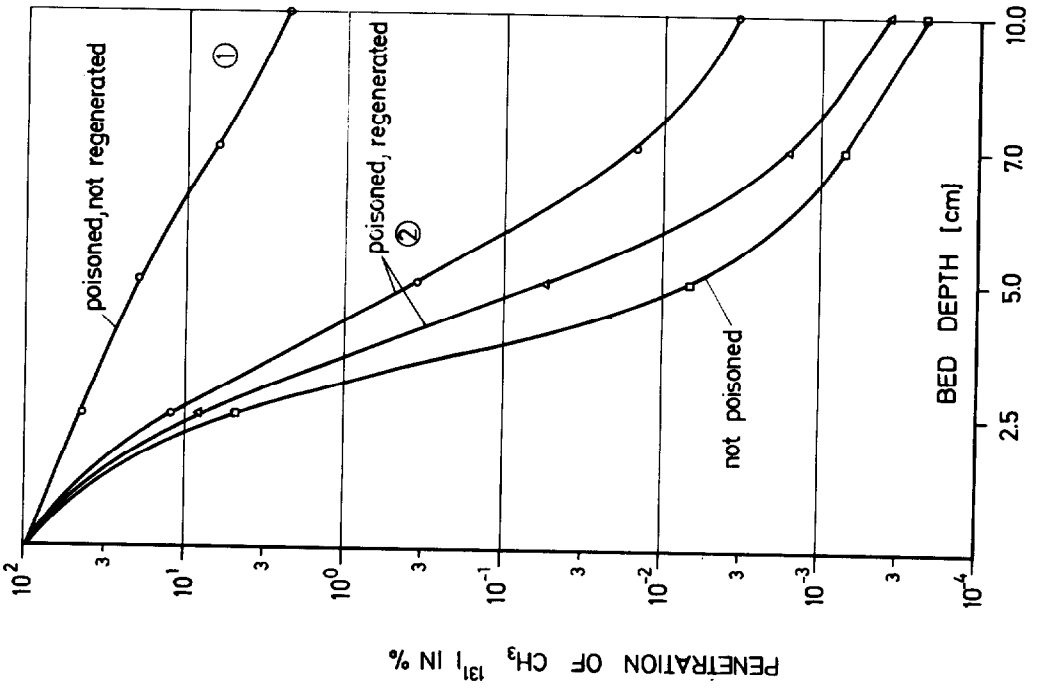
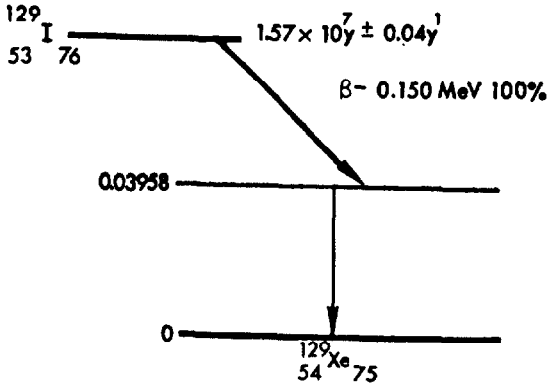


FIG. 10 Penetration of AC 6120 test beds by CH_3 ^{131}I after use in vessel off-gas and after regeneration with NO_2.

Notes on Iodine-129 (copied from NBS Certificate)

Decay Scheme



Radiation	Energy (MeV)	Intensity (%)	Relative Intensity to $K\alpha_1$	Conversion Coefficients	ω_K
γ	0.03958±0.0003 (1)	7.52		α_K 10.5 $\alpha_{L,M}$ 1.8 α_T 12.3 (1)	
$x(K\alpha_1)$	0.02978	37.0	1		(4) 0.889±0.020
$x(K\alpha_2)$	0.029458	19.9	0.537		
$x(K\beta_1^1)$	0.03360	10.8	0.292		
$x(K\beta_2^1)$	0.03442 (2)	2.4	0.064 (3)		
β-	0.150±0.005 (1)				

1. Nuclear Data Sheets, Vol. 8, No. 2, August, 1972.

2. NSRDS-NBS14: X-Ray Wavelengths and X-Ray Energy Levels.

3. Atomic Data, Nov., 1970.

4. Reviews of Modern Physics 44. 716, 1972.

FIG. 12

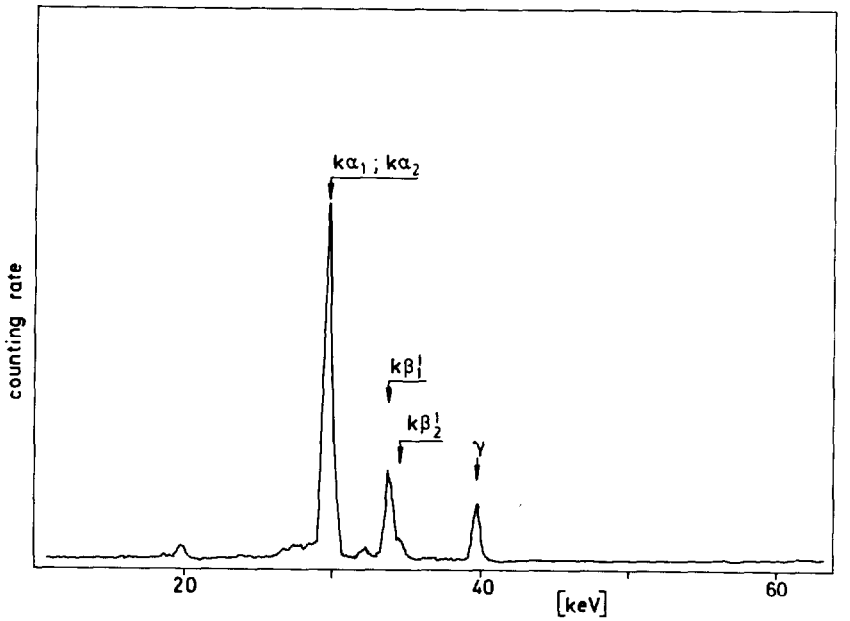


Fig. 13 γ/X-ray spectrum of 1 ml of NBS standard solution SRM 4949 with 2×10^{-8} Ci ^{129}I

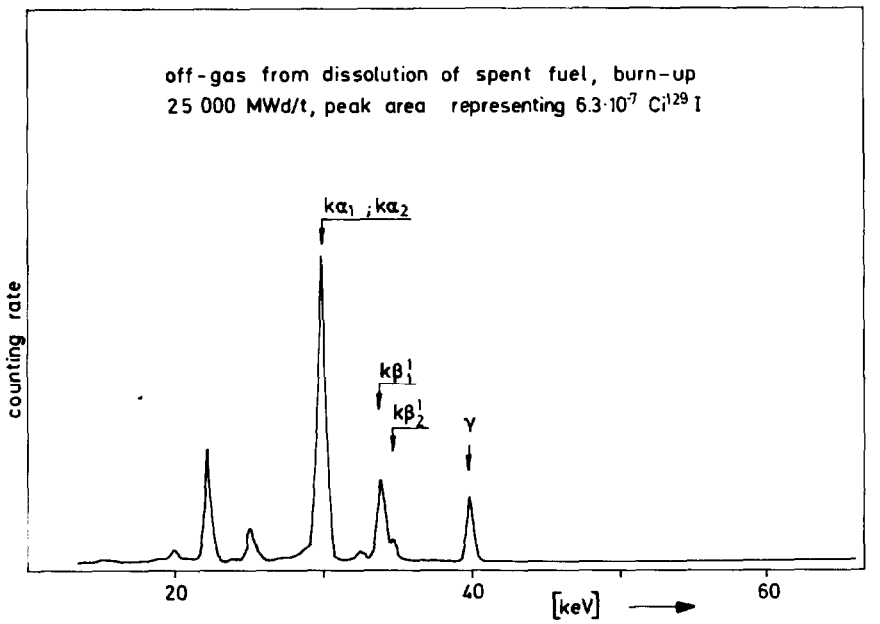


Fig. 14 γ/X-ray spectrum of an AC 6120 sample loaded with ^{129}I

Tab. I Removal of ^{131}I in form of $CH_3{}^{131}I$ by commercially produced AC 6120

Conditions:

Ag content of sorption material	: 7 wt.%
grain size	: 1 - 2 mm
Sweep gas	: humid air, dew point: 30°C
temperature of sweep gas and test bed	: 150°C
linear air velocity	: 25 cm/s
Loading	: 1.1 mg $CH_3{}^{127}I$ + 6 µCi $CH_3{}^{131}I$ per g of AC 6120, loading period: 1 h

bed depth (cm)	2.5	5.0	7.5	10.0
residence time (s)	0.1	0.2	0.3	0.4
removal efficiency (%)	99.85	99.999	99.9995	99.9997

Tab. II Removal of ^{131}I in form of $CH_3{}^{131}I$ by commercially produced AC 6120/H_1

Conditions:

Ag content of sorption material	: 12 wt.%
grain size	: 1 - 2 mm
Sweep gas	: humid air, dew point: 30°C
temperature sweep gas and test bed	: 150°C
linear air velocity	: 25 cm/s
Loading	: 1 mg $CH_3{}^{127}I$ + 5 µCi $CH_3{}^{131}I$ per g of AC 6120, loading period: 1 h

bed depth (cm)	2.5	5.0	7.5	10.0
residence time (s)	0.1	0.2	0.3	0.4
removal efficiency (%)	99.975	99.9956	99.9989	99.9998

Tab. III Removal of iodine from dissolver off-gas of SAP Marcoule by use of AC 6120/H_1

Bed depth: 35 cm, Temperature of off-gas and test bed: 150°C, residence time: 1.6 s.
Concentration of iodine in dissolver off-gas, averaged over period of dissolution: ∿ 4.5 g/m^3

No.	loading time [h]	off-gas volume [m^3]	$K^{127}I$ spiking of feed solution [g]	Position of test bed relativ to NO_2-absorption column	^{131}I-removal efficiency [%]
1	2	3	44.5	downstream	99.998
2	7 (9.0)*)	10.5	42	upstream	99.9992
3	6.5 (15.5)	9.75	52	upstream	99.994
4	6.25(21.75)	9.4	0	downstream	99.995
5	8.5	12.75	52	downstream	99.96
6	8.5 (17.0)	12.75	52	downstream	99.996
7	6.75(23.75)	10.1	52	upstream	99.999
8	7.0 (30.75)	10.5	52	downstream	99.994

*) bracketed values: cumulative loading time of successive loading periods

Tab. IV Removal of iodine by an AC 6120/H_1 test bed of proposed bed depth for a large reprocessing plant. Sweep gas: humid air + 1 % NO_2, 150°C

Grain size of iodine sorption material: 1 - 2 mm
dew point of humid air : 30°C, preconditioning: 20 h, loading period: 4 h
sweep gas continued for an additional : 4 h. Loading 18.1 g I_2
mixed with : 1.04 mCi ^{131}I

data for accumulated bed depth			data for single section of test bed			
% of total bed depth	^{131}I removal efficiency [%]	I_2 loading [mg]	No. of test bed section	I_2 loading [mg]	reacted amount of Ag [mg]	Ag reacted in % of Ag inventory
6.6	10.9	1970	1.	1970	1680	87.7
13.1	22.0	3980	2.	2010	1710	89.3
19.7	33.0	5970	3.	1990	1690	88.4
26.3	44.0	7960	4.	1990	1690	88.4
32.9	55.0	9950	5.	1990	1690	88.4
39.5	65.7	11890	6.	1940	1650	86.0
46.0	75.6	13680	7.	1790	1520	80.1
52.6	84.0	15200	8.	1520	1290	67.5
59.2	91.2	16510	9.	1310	1110	57.9
65.8	96.5	17469	10.	959	815	42.6
72.3	99.4	17994	11.	525	446	23.3
78.9	99.9964	18099	12.	105	92	4.8
85.5	99.9994	18100	13.	0.5	0.4	0.02
92.1	99.9995	-	14.	+)	+)	+)
100.0	99.9998	-	15.	+)	+)	+)

+) falling below detection limit

Tab. V Removal of iodine by an AC 6120/H_1 test bed of proposed bed depth for a large reprocessing plant. Sweep gas: humid air + 2,5 % NO_2, 150°C

Grain size of iodine sorption material: 1 - 2 mm
dew point of humid air : 30°C, preconditioning: 20 h, loading period: 5 h
sweep gas continued for an additional : 12 h. Loading 18.1 g I_2
mixed with : 0.55 mCi ^{131}I

data for accumulated bed depth			data for single section of test bed			
% of total bed depth	^{131}I removal efficiency [%]	I_2 loading [mg]	No. of test bed section	I_2 loading [mg]	reacted amount of Ag [mg]	Ag reacted in % of Ag inventory
6.6	11.4	2070	1.	2070	1760	94.3
13.1	22.5	4080	2.	2010	1710	91.6
19.7	33.4	6050	3.	1970	1670	89.7
26.3	44.0	7970	4.	1920	1630	87.5
32.9	54.1	9790	5.	1820	1540	82.7
39.5	63.5	11490	6.	1700	1450	77.5
46.0	72.3	13090	7.	1600	1360	72.8
52.6	80.1	14490	8.	1400	1190	63.9
59.2	86.8	15710	9.	1220	1040	55.7
65.8	92.2	16684	10.	974	828	44.4
72.3	96.0	17366	11.	682	580	31.1
78.9	98.3	17782	12.	416	354	19.0
85.5	99.5	18003	13.	221	188	10.1
92.1	99.903	18080	14.	74	63	3.4
100.0	99.9987	18096	15.	16	14	0.8

Tab. VI Removal of iodine by an AC 6120/H_1 test bed of proposed bed depth for a large reprocessing plant. Sweep gas: humid air 5 % NO_2, 150°C

Grain size of iodine sorption material: 1 - 2 mm
dew point of humid air : 30°C, preconditioning: 20 h, loading period: 5 h
sweep gas continued for an additional : 4 h. Loading 18.1 g I_2
mixed with : 1 mCi ^{131}I

data for accumulated bed depth			data for single section of test bed			
% of total bed depth	^{131}I removal efficiency [%]	I_2 loading [mg]	No. of test bed section	I_2 loading [mg]	reacted amount of Ag [mg]	Ag reacted in % of Ag inventory
6.6	10.9	1960	1.	1960	1670	94.2
13.1	21.8	3940	2.	1980	1680	95.0
19.7	32.7	5910	3.	1970	1680	94.6
26.3	43.4	7850	4.	1940	1640	92.8
32.9	54.1	9790	5.	1940	1650	92.9
39.5	64.7	11720	6.	1930	1640	92.5
46.0	75.2	13610	7.	1890	1610	90.8
52.6	85.2	15420	8.	1810	1540	87.1
59.2	91.2	16500	9.	1080	917	51.7
65.8	95.5	17276	10.	776	660	32.2
72.3	98.3	17785	11.	509	433	24.4
78.9	99.7	18035	12.	250	213	12.0
85.5	99.9901	18091	13.	56	48	2.7
92.1	99.9990	18093	14.	2	2	0.1
100.0	99.9997	18094	15.	1	1	-

Tab. VII Removal of iodine by an AC 6120/H_1 test bed of proposed bed depth for a large reprocessing plant. Sweep gas: humid air 5 % NO_2, 120°C

Grain size of iodine sorption material: 1 - 2 mm
dew point of humid air : 30°C, preconditioning: 20 h, loading period: 5 h
sweep gas continued for an additional : 4 h. Loading 18.1 g I_2
mixed with : 1.04 mCi ^{131}I

data for accumulated bed depth			data for single section of test bed			
% of total bed depth	^{131}I removal efficiency [%]	I_2 loading [mg]	No. of test bed section	I_2 loading [mg]	reacted amount of Ag [mg]	Ag reacted in % of Ag inventory
6.6	10.5	1900	1.	1900	1620	91.4
13.1	20.6	3720	2.	1820	1550	87.5
19.7	30.5	5510	3.	1790	1520	86.0
26.3	40.0	7220	4.	1710	1450	82.1
32.9	49.1	8880	5.	1660	1410	80.0
39.5	57.8	10460	6.	1580	1340	75.8
46.0	66.0	11940	7.	1480	1260	71.1
52.6	74.1	13400	8.	1460	1240	69.9
59.2	81.5	14740	9.	1340	1140	64.5
65.8	88.4	16000	10.	1260	1070	60.3
72.3	94.0	17010	11.	1010	850	48.5
78.9	97.8	17692	12.	682	580	32.8
85.5	99.6	18012	13.	320	272	15.4
92.1	99.9936	18088	14.	76	65	3.7
100.0	99.9998	18090	15.	2	2	0.1

Tab. VIII Removal of iodine by a test bed out of molecular sieve type 13 X-Ag. Proposed bed depth for a large reprocessing plant, sweep gas: humid air + 5 % NO_2, 150°C

Grain size of iodine sorption material: 1 - 2 mm
dew point humid air : 30°C, preconditioning: 20 h, loading period: 4 h
sweep gas continued for an additional : 4 h. Loading: 18.1 g I_2
mixed with : 1.57 mCi ^{131}I

data for accumulated bed depth			data for single section of test bed			
% of total bed depth	^{131}I removal efficiency [%]	I_2 loading [mg]	No. of test bed section	I_2 loading [mg]	reacted amount of Ag [mg]	Ag reacted in % of Ag inventory
6.6	21.6	3910	1.	3910	3320	35.2
13.1	44.0	7970	2.	4060	3450	36.5
19.7	63.6	11520	3.	3550	3010	32.0
26.3	81.0	14660	4.	3140	2670	28.2
32.9	93.6	16950	5.	2290	1950	20.6
39.5	99.6	18030	6.	1080	920	9.7
46.0	99.9994	18100	7.	70	61	0.6
52.6	*) > 99.999	-	8.	-	-	-
59.2	*) > 99.999	-	9.	-	-	-

*) below detection limit

Tab. IX Removal of iodine by a test bed made of molecular sieve, type 13 X-Ag. Proposed bed depth for a large reprocessing plant, sweep gas: humid air, 150°C

Grain size of iodine sorption material: 1 - 2 mm
dew point humid air : 30°C, preconditioning: 20 h, loading period: 4 h
sweep gas continued for an additional : 20 h. Loading 36.2 g I_2
mixed with : 1.41 mCi ^{131}I

data for accumulated bed depth			data for single section of test bed			
% of total bed depth	^{131}I removal efficiency [%]	I_2 loading [mg]	No. of test bed section	I_2 loading [mg]	reacted amount of Ag [mg]	Ag reacted in % of Ag inventory
6.6	17.3	6270	1.	6270	5330	56.4
13.1	33.6	12160	2.	5890	5010	53.0
19.7	48.8	17670	3.	5510	4680	49.5
26.3	62.9	22800	4.	5130	4370	46.2
32.9	75.6	27380	5.	4580	3890	41.1
39.5	86.5	31330	6.	3950	3360	35.5
46.0	94.7	34290	7.	2960	2520	26.7
52.6	99.1	35890	8.	1600	1360	14.4
59.2	99.9992	36200	9.	310	260	2.8
65.8	99.9999	36200	10.	0.3	0.3	$3 \cdot 10^{-3}$
72.3	*) >99.9999	-	11.	-	-	-
78.9	*) >99.9999	-	12.	-	-	-

*) below detection limit

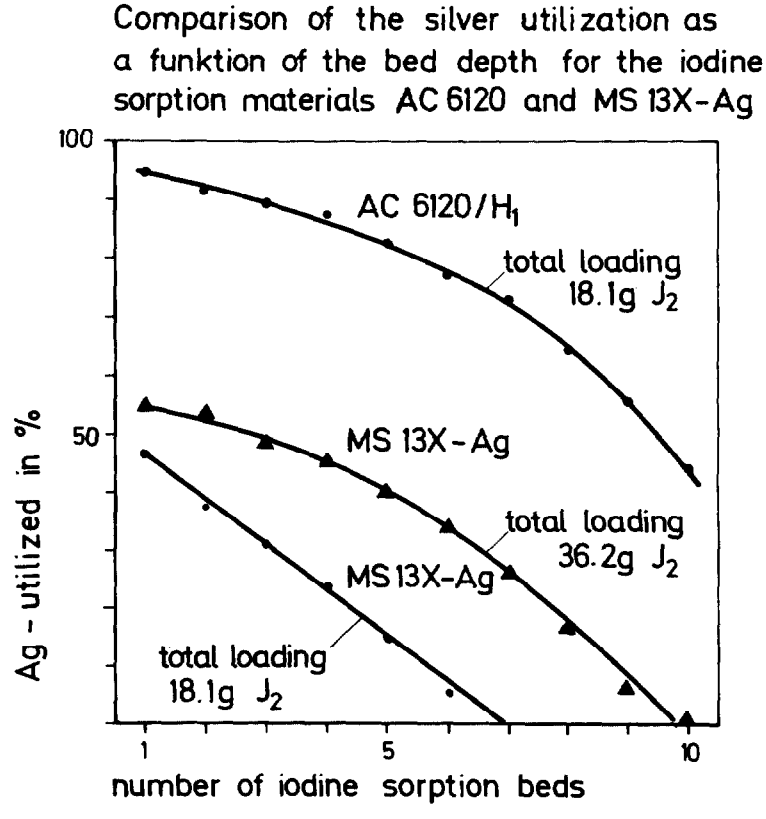
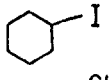
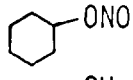
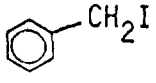
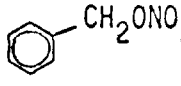
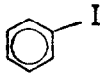


FIG. 15

Tab. X Reactions of AC 6120 with gaseous organic iodine compounds

Compound	Reaction products
CH_3I	AgI, CH_3ONO_2, alkanes
C_2H_5I	AgI, $C_2H_5ONO_2$
.	.
.	.
$C_{12}H_{25}I$	AgI, $C_{12}H_{25}ONO_2$
CH_3-CHI-CH_2-CH_3	AgI, H_3C-CH=CH-CH_3, H_2C=CH-CH_2-CH_3, HNO_3
$(CH_3)_3$ CI	AgI, $(CH_3)_2$-C=CH_2, $C_nH_{2n+1}I$
	AgI,  , HNO_3
	AgI, 
	no reaction up to 180°C

DISCUSSION

PARKER: Is the concentration of TBP in the air stream in the pilot plant representative of what you might find in reprocessing fac ilities, or are you just guessing?

WILHELM: The filters tested had been installed in an operating reprocessing plant. We obtained the iodine removal data with contaminants produced under operational conditions.

PARKER: Is it representative of what you might find in a full scale reprocessing plant?

WILHELM: I think so.

MURBACH: What is AC-6120?

WILHELM: It is amorphous silicic acid with a special pore structure, impregnated with 7% $AgNO_3$ by weight (12% for AC-6120/H1).

DEITZ: Have other impregnations than $AgNO_3$ been tested on AC-6120?

WILHELM: AC-6120 identifies an $AgNO_3$ impregnated material. The base material has been impregnated with other impregnants, but the results were not as good as with $AgNO_3$.

SKOLRUD: During the AC-6120 regeneration step, do only the phosphate compounds (as contaminants) desorb?

WILHELM: The main regeneration effect is the transformation of elemental Ag and Ag_2O, which are the reaction products of reduction processes with organic compounds, to $AgNO_3$. I do not know whether the Ag_3PO_4 reacts with NO_2, but after regeneration, the performance of the material is so fully restored that apparently Ag_3PO_4 causes no difficulties.

SKOLRUD: What is the NO_2 content during regeneration?

WILHELM: We used 2.5% NO_2 in the process.

GOVERNMENT-INDUSTRY CONFERENCE ON ADSORBERS AND ADSORPTION MEDIA

C. A. Burchsted
Secretary, Government-Industry Conference

The Government-Industry Conference on Adsorbers and Adsorption Media met at Washington, D.C., on March 25, 1976, with M. W. First (HACL) presiding. Jack Dempsey, ERDA, gave the welcome and also outlined the program for the 14th ERDA Air Cleaning Conference to be held in Sun Valley, Idaho, in August.

V. R. Deitz, Naval Research Laboratory

Deitz reported on Phase III of the Domestic Carbon Program. This program was undertaken several years ago under the urging and direction of Humphrey Gilbert, USAEC, to identify suitable domestically available base materials for nuclear grade activated carbon. In Phase I, C. A. Burchsted, ORNL, surveyed the carbon industry and selected a number of promising materials for further investigation. In Phase II, the properties and ability to impregnate these materials were studied.* In Phase III, Deitz investigated the mechanisms involved in radioiodine trapping by adsorbents and the role of the base carbon. A two-stage impregnation procedure using salts of iodine oxyacids, I_2, and/or KI in the first stage and hexamethyltetramine (HMTA), a high-flash-point tertiary amine, in the second, was developed. The results were comparable to the best TEDA-KI-impregnated coconut carbons, but with more favorable (higher) ignition temperature. It was found that the smaller iodine molecules must be put on the carbon first, then the larger HMTA molecules; the procedure cannot be reversed. Patents have been applied for by ERDA. Confirmatory tests were made by Evans (SRL) and Rivers (AAF).

Deitz described the chemistry of the new impregnation method and the mechanism of radioiodine trapping and retention. He believes that radioiodine trapping by adsorbers is a catalytic process (as opposed to the isotopic exchange and chemical reaction mechanisms currently in vogue) with CH_3I reacting with the reactive species placed on the carbon in a chain reaction. The carbon serves primarily as a catalyst support, although it is probably not completely inert in the reaction. The chain reaction can be killed by acidification, either by reaction products, poisons inherent in the carbon itself, or poisons collected from the air stream. The base carbon serves as a sink for the reaction products, but can become poisoned if they become excessive. Deitz found a dependence of radioiodine effectiveness on bed depth (to be reported at the 14th Air Cleaning Conference), velocity (at constant gas residence time), pH, and I_2-to-KI content of the base carbon/impregnant complex. The spontaneous ignition and desorption temperatures of

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* V. R. Deitz and C. A. Burchsted, *Survey of Domestic Charcoals for Iodine Retention*, NRL Memorandum Report 2960, Naval Research Lab.

the HMTA-impregnated carbons were greater than 430°C and 200°C, respectively, for all base materials. Base materials included coal, petroleum, wood, and nut carbons, in addition to coconut used as a "control." Deitz concluded that a satisfactory base material must:

- have a large surface area (> 1000 m^2/g) to support the impregnants.
- support a high pH (water extract) to protect the impregnants.
- have an optimum particle size distribution and hardness.
- have sufficient macropore volume to transport radioiodine and reaction products to "active sites" on the surface.
- have sufficient excess surface area to accommodate contaminants expected under service conditions.
- have high ignition and impregnant-desorption temperatures.
- have with proper impregnation good radioiodine effectiveness at high RH.

A. G. Evans, Savannah River Laboratory

Evans reported on the application of the new impregnation method to a variety of base materials. He found it possible to successfully impregnate any satisfactory base material by adjusting the HMTA, iodine, and flame-retardent contents of the impregnant. Reproducibility of the two-stage impregnation was good when the base carbon was consistent from lot to lot, and radiolytic iodine desorption of the better combinations were comparable to those of the best current carbons. Evans found that there must be sufficient excess alkalinity in the impregnant and/or natural alkalinity of the base carbon to maintain proper pH. It was also found that the iodine/potassium ratio is critical to the formation of oxyiodine salts that can be retained by the carbon.

Work at SRL verifies that close control of particle size and particle size distribution in original purchase is essential for satisfactory performance and good service life. With respect to service aging and weathering, smaller particles were superior from the standpoints of both CH_3I and radiation penetration over a period of service and suffer less breakdown in service. (Note: the importance of close control over particle size and particle size distribution was discussed by Evans and Dr. Wilhelm at the last meeting of the Government-Industry Conference.)

Studies of used carbons from the Savannah River confinement systems showed a dramatic drop in pH of water extract after exposure to service conditions (from a pH of 9 to 10 new to a pH of 5-6 over a period of 12 to 20 months). It is possible that monitoring of the pH of the water extract may be a means of monitoring the useful life of the carbon. The drop in pH results from poisoning due to contaminants removed from the air. Evans noted a

continuous increase in chloride content, probably due to chlorinated compounds, but the effect of this on pH is unknown. It is known that SO_2 and NO_x reduces pH and poisons the carbon. There is also a decrease in ignition temperature with aging. Dr. Wilhelm noted that much of the solvents may result from the curing of paints in operating areas of the plant. Surface area also decreases with service aging. Although surface area is regenerable, pH, ignition temperature, and poisoning effects are not reversible.

J. T. Collins, R. R. Bellamy, U. S. Nuclear Regulatory Commission

Collins discussed the philosophy of the NRC position, noting several criteria (Nos. 41, 42, and 43; and 19 and 51) of 10-CFR-50 Appendix A which deal with mitigation of the consequences of an accident and release under normal operation, that Appendix I provides numerical guides for implementation of ALARA, and that only Branch Technical Positions pertaining to air cleaning systems are available for guidance for non-ESF systems. Bellamy discussed NRC's Standard Review Plans and what is looked for in the review of Safety Analysis Reports. NRC recommends carbon adsorbers in ESF systems, in offgas and holdup systems, and in non-ESF normal ventilation systems. Copies of tables from Regulatory Guide 1.52 and the Branch Technical Position for non-ESF systems were passed out (see attachments). The BTP essentially downgrades the recommended requirements for carbon for non-ESF systems from that recommended for ESF systems. The new issue of Regulatory Guide 1.52 will be out this summer. Bellamy also noted that source term calculation procedures are given in Nuclear Regulatory Reports 75-0016 and -009. The new issue of Regulatory Guide 1.52 still recommends sampling and laboratory testing of carbons from ESF systems every 720 hours of filter system operation or annually, whichever is less. As noted by Evans, aging and weathering of carbon is a site-specific parameter, and the recommendation to test every 720 hours of system operation is considered conservative. Activated carbon is not actually required in ESF systems, and alternatives will be considered and can be approved by NRC. The 95% ball-pan hardness value is specified by NRC because of the substantial carbon attrition experienced in some adsorption systems. Kovach (Nuclear Consulting Services) noted that some of this attrition may result from inadequate filling of adsorber cells. A representative of Mine Safety Appliances Company questioned the validity of the 95% hardness specification.

Dr. Jurgen Wilhem, Karisruhe, Germany

Wilhelm described a German adsorption system which has two stages of activated carbon. The first stage is loaded with an unimpregnated carbon and serves as a guard bed for the second stage of impregnated carbon. The first stage is unheated (heating of the first stage would simply drive the petroleum base and low boiling point compounds captured in it into the second stage). Provision is made for periodic heating of the second stage to drive off higher boiling point compounds (poisons) not caught in the first stage. The arrangement has been used successfully to restore the effectiveness of the second stage carbon after a period of use and to extend the useful life of the system.

Wilhelm discussed round-robin testing of carbons in Europe. The proposed European-U.S. round-robin program proposed after the Karlsruhe meeting in 1973 was inconclusive, but did indicate the need to test the laboratories rather than carbons *per se*. A subsequent round-robin in Europe employed uniform samples of Norit, Sutcliffe-Speakman, and a French carbon tested under the following conditions:

Temperature	30°C
Relative Humidity	95%
Bed Size	2.5 cm dia x 5 cm deep
CH_3I Concentration	50 μg CH_3I/gC
Airflow Velocity	25 cm/s
Preequilibration Period	16 h
Loading Period	60 m
Elution Period	1 - 2 h

A second test was made with RH = 98-100%. A face-to-face meeting of the participants was held before this second series with the results that test values of the various laboratories were close. Wilhelm stressed the need for face-to-face meetings if such round-robins are to be successful. The round-robin indicated that test bed diameter is not a significant parameter, but apparent density (AD) is. A final report of the European test program is at least two years away.

Germany bases acceptance of activated carbon on a K factor where:

$$K = \frac{\log DF}{\dagger}$$

where,

DF = decontamination factor.

† = gas-residence time = bulk volume divided by volume airflow.

A K value of 5, minimum, is considered acceptable. The K factor for the European round-robin tests showed variances that cannot be explained yet. Obviously, AD is important and must be very accurately determined.

J. L. Kovach, Nuclear Containment Systems

Kovach reported on NCS testing of new and used carbons. The tests show that used carbon samples should not be preequilibrated when making iodine and methyl iodide "efficiency" tests. Preequilibration of used carbon in effect regenerates them and gives incorrect test results. NCS found up to 160 different compounds coming off unimpregnated carbons even before they had been exposed to the service environment. Tests of coal-base carbons gave off substantial quantities of sulfur as SO_2; as much as 0.2% as sulfur in new carbons and 3.5% in aged carbons.

Kovach also commented on variation of carbon samplers used in current systems and stressed the need for greater uniformity of design. Results of iodine and methyl iodide "efficiency" tests of carbons from widely varying sampler and sampler-installation designs are difficult, if not impossible, to correlate.

NCS reports many instances of significant settling observed in carbon cells in operating adsorption systems. Kovach recommended that cells be vibrated at the natural frequency of the cells during filling to alleviate the problem. He noted that sampler cartridges are generally better packed than cells of the system, which results in iodine and methyl iodide test results that are not representative of the actual system. He recommended that any one adsorption system be filled with carbon from the same manufacturing batch; the use of several batches in the same system gives poor results. Also, there is a definite correlation between the amount of dusting from cells and the orientation of screen perforations. He recommended to cell manufacturers that the rough surfaces of screens (due to perforating operation) be on the outside of the beds.

For used carbon, Kovach recommended that a test temperature of 20°C with no preequilibration be used. This was noted by the ASTM D28 Committee members present.

F. R. Schwartz, North American Carbon Company

Schwartz reported on an investigation of carbon particle degradation. The current test methods (ball-pan, dust elutriation, T-bar stirring) do not measure degradiation accurately and test results can seldom be correlated with field use. Schwartz gave the ASTM definitions of "abrasion resistance," "crushing strength," and "hardness" (see ASTM D2652) and showed that the forces involved in degradation are different than those actually measured by the currently recognized tests. NAC is currently developing new tests that will be made available to the industry, one that measures abrasion resistance, the other to measure crushing strength. The work to date on these tests indicates that both tests can distinguish between granular carbons with respect to their ability to resist abrasion and crushing forces and seem to be independent of particle size and geometry effects and appear to correlate with field experience. (Note: ASTM D-28 Committee at its annual meeting in Chicago in June 1976 decided against submitting any of the currently recognized tests as methods for measuring abrasion resistance at this time. The method for the ball-pan hardness test was submitted for ballot, but simply as a test for a measurable property of carbon for comparison purposes.)

C. A. Burchsted, Union Carbide Corporation, Oak Ridge, Tennessee

Burchsted summarized the status of current standards relating to activated carbon and adsorption systems:

ANSI N509	*Requirements for Nuclear Power Plant Air Cleaning Units and Components*	Will probably be issued in summer 1976

ANSI N510	*Testing of Nuclear Air Cleaning Systems*	Issued
AACC CS-8	*High-Efficiency Gas-Phase Adsorber Cells*	Revision in Progress
RDT M16-1	*Gas-Phase Adsorbents for Trapping Radioactive Iodine and Iodine Compounds*	Revision in Progress
ASTM D2652	*Definitions of Terms Relating to Activated Carbon*	Issued Reaffirmed
ASTM D2854	*Test for Apparent Density of Activated Carbon*	Issued Reaffirmed
ASTM D2862	*Test for Particle Size Distribution of Granulated Activated Carbon*	Issued Reaffirmed
ASTM D2866	*Test for Total Ash Content of Activated Carbon*	Issued Reaffirmed
ASTM D2867	*Test for Moisture in Activated Carbon*	Issued
ASTM D3466	*Test for Ignition Temperature of Activated Carbon*	Approved for Issue
ASTM D3467	*Test for Carbon Tetrachloride Activity of Activated Carbon*	To be issued summer 1976
ASTM D----	*Radioiodine Testing of Nuclear Grade Gas-Phase Adsorbents*	Committee Ballot July 1976

R. A. Lorenz, Oak Ridge National Laboratory

Lorenz summarized findings of the Oak Ridge work on auto-ignition of activated carbon due to fission-product heating. At low airflow velocity through the bed there is no "break away" temperature rise to indicate the occurrence of ignition, so ignition is defined as the temperature corresponding to a rate of rise of 20°C/m. This temperature corresponds to a heat release rate (primarily due to oxidation) of 15 cal/g of carbon/min. For air velocities below 2 fpm, the rate of oxidation heat release decreases following ignition and carbon-bed temperature stabilizes at about 400°C. An increase in airflow velocity results in higher heat-release rate and higher bed temperature. At low airflow velocities, significant iodine desorption did not result from bed heatup and ignition at any time during the ORNL tests; it is concluded, therefore, that time is available in the event of an adsorption system fire to carry out fire extinguishment operations if suitable fire extinguishing techniques can be developed.

The ORNL tests indicated that a highly penetrating form of radioiodine (HOI ?) is continuously formed and released from an adsorption system in a radiation field. The rate of formation

and release is apparently dependent on moisture and radioation intensity and is independent of carbon-bed temperature (between 70°C and 400°C), airflow velocity (between 2 and 28 fpm), carbon base material, impregnant, and adsorbed contaminants (paint fumes, etc). The partition coefficient of this penetrating species in water is less than 10, but higher in CCl_4. The collection efficiency of the species at 130°C is poor for activated carbon but about 20 to 50 times better for silver-exchanged zeolite. Collection on silver nitrate coated adsorbers at 130°C is also poor. The species will sorb on both activated carbon and silver-zeolite at - 78°C.

The ORNL work also confirms the finding, reported at previous G-I Conference meetings, that sorption of radioiodine as CH_3I is a function of airflow velocity through the bed with constant gas residence time. A comparison of work by Ackley (ORNL) and Underhill (HACL) using ^{85}Kr indicates that there is a minimum collection efficiency at about 0.2 to 0.8 cm/sec.

J. F. Fish, American Air Filter Company

Fish, who is chairman of the ASME Committee on Nuclear Air and Gas Treatment (CONAGT) presented the case for qualification of field testing personnel. CONAGT has made provision for a subcommittee on qualification of field test personnel in view of the proliferation of testing agencies, some of whom appear to have limited competence in the field. It was proposed that Harvard Air Cleaning Laboratory might conduct the qualification activity for ERDA or NRC. Fish also recommended the qualification of testing laboratories and proposed that any such laboratory be sanctioned by NRC. Such laboratories would be required to periodically requalify by making tests on standardized samples prepared by NRL or an ERDA facility such as ORNL or SRL. One sample would be new, unused material, another would be taken from a system in which it had been exposed to service environment. Comparison of test results would indicate problems with respect to procedure, technique, and other laboratory-sensitive conditions. Fish pointed out that there is a precedent for such action in the HEPA filter Quality Assurance program operated by ERDA at Oak Ridge, Hanford, and Rocky Flats. Such a program approaches Government licensing and in some respects functions as a "Bureau of Standards" for this area. The benefit would be the assurance to NRC and plant operators that the data developed to verify the efficacy of on-line systems is valid under the test conditions imposed.

TABLE 2 FROM PROPOSED REGULATORY GUIDE

SUMMARY TABLE OF NEW ACTIVATED CARBON PHYSICAL PROPERTIES
Batch Tests to be Performed on Finished Adsorbent
(Recommendations for Out-Of-Containment Systems)

	TEST	ACCEPTABLE TEST METHOD	ACCEPTABLE RESULTS
1.	Particle Size Distribution	ASTM D2862 (Ref. 28)	Retained on #6 ASTM E11 (Ref. 29) Sieve: 0.0% Retained on #8 ASTM E11 (Ref. 29) Sieve: 5.0% Maximum Through #8, retained on #12 Sieve: 40% to 60% Through #12, retained on #16 Sieve: 40% to 60% Through #16 ASTM E11 (Ref. 29) Sieve: 5.0% max. Through #18 ASTM E11 (Ref. 29) Sieve: 1.0% max.
2.	Hardness Number	RDT M16-1T, Appendix C (Ref. 30)	95 minimum
3.	Ignition Temperature	RDT M16-1T, Appendix C (Ref. 30)	330°C minimum at 100 fpm
4.	Activity	CCl_4 Activity, RDT M16-1T, Appendix C (Ref. 30)	60 minimum
5.	Radioiodine Removal Efficiency		
	a. Methyl Iodide, 25°C and 95% Relative Humidity	RDT M16-1T (Ref. 30), para. 4.5.3, except 95% relative humidity air is required.	99%
	b. Methyl Iodide, 80°C and 95% Relative Humidity	RDT M16-1T, (Ref. 30), para 4.5.3, except 80°C and 95% relative humidity air is required for test (pre- and post-loading sweep medium is 25°C)	99%
	c. Methyl Iodide, in Containment	RDT M16-1T, (Ref. 30), para. 4.5.4, except duration is 2 hours at 3.7 atm. pressure	98%
	Radioiodine Removal Efficiency (Cont'd)		
	d. Elemental Iodine Retention	Savannah River Laboratory (Ref. 31)	99.9% loading 99% loading plus elution
6.	Bulk Density	ASTM D2854 (Ref. 32)	0.38 gm/ml minimum
7.	Impregnant Content	State Procedure	State type (not to exceed 5% by weight)

NOTES:

(1) A batch test is defined as a test made on a production batch of product to establish suitability for a specific application. A batch of activated carbon is defined as that quantity of the same grade, type, and series of material which has been homogenized to exhibit, within reasonable tolerance, the same performance and physical characteristics; and for which the manufacturer can demonstrate by acceptable tests and quality control practices such uniformity. All material in the same batch shall be activated, impregnated, and otherwise treated under the same process conditions and procedures, in the same process equipment, and shall be produced under the same manufacturing release and instructions. Material produced in the same charge of batch-type equipment shall constitute a batch; material produced in different charges of the same batch-type equipment may be included in the same batch only if it can be homogenized as above. The maximum batch size shall be 350 cu. ft. of activated carbon.

(2) Test 4 should be performed on base material.

(3) Test 5a should be performed for qualification purposes. A qualification test is a test which establishes the suitability of a product for a general application, normally a one-time test reflecting historical typical performance of material.

(4) Test 5c should be performed for qualification purposes on carbon to be installed in primary containment (recirculating) atmosphere cleanup systems.

CLOSING REMARKS OF SESSION CHAIRMAN: (R. D. Rivers)

This morning when Mr. W. H. Hannum stated the aims of this conference he said he hoped that we would actually be learning something. I think this session indicates that we are, but that the process of learning is never easy. We move from mere reporting of results and performance, from attempts to find something that somehow works, to far more detailed understandings of the processes and conditions under which things will operate.

I emphasize the word "detail". A fraction of a per cent of impregnant here, a sequence of impregnation there, a pattern of equilibration in test procedures, the exact sequence of adsorption media in a sampling train - all of these things influence our thinking, our results, the development of our materials and methods.

Jurgen Wilhelm in his introductory remarks has summarized the papers given, and I think there have been no surprises. I will confine these remarks to the controversies that arose, and try to summarize where this set of papers places us.

A recurrent them here has been: How do we determine the present condition of a bank of carbon that has been in service, and what will its remaining life be? Strauss and Deckers both found problems in the first step to answer this question: obtaining a sample representative of the full-scale system being examined. Their questionners seemed to say problems were exaggerated, and that explanations-and cures - could be found for the anomalies Strauss and Deckers observed. Assuming these problems can be overcome, we must decide how to test a given sample. Hunt's observations of the regenerative effects of equilibration of aged carbon was not challenged, though Deitz promises to give some contradictory data for <u>new</u> carbons in Session 9; possibly the two effects counter each other at some point. The data reported by Evans on used carbons shows very high

penetration values, in spite of 16-hour equilibration before testing. It is possible that penetrations would have been greater if Evans had not pre-equilibrated. Parrish described a procedure for relating the ultimate life of a carbon bed to data obtained early in its life. The strength of the correlations he showed were indeed remarkable, considering the wide variation in ambient contaminants observed around nuclear plants. If this technique can be shown reliable in other locales than those which gave Parish's correlations, it will indeed be a useful method for it also allows life prediction for different bed depths.

Jonas delved into the same area from a more detailed, theoretical viewpoint, showing that the "rate constant" for radiomethyliodide capture by several impregnated carbons is proportional to the square root of the superficial bed velocity. The dependence of this rate constant on particle size did not agree with earlier studies. Jonas' contention that the data indicate catalysis as the controlling surface phenomenon may well be true. The argument would be more pursuasive if the observed rate constants (which, incidentally, include mass transfer effects) do not decline with long bed exposure. Deckers and Sigli offer a way to avoid prediction to some extent: measure current bed performance using radioiodine compounds. The concept has been reported before; their equipment shows admirable attention to safety and convenience. They admit, however, that they cannot by their test tell what an adsorber will do under accident conditions. Humidity and temperature have serious effects, and Lorenz documents still another, radiation. Heating and ignition were observed, and radiolytic generation of as yet uncharacterized radioiodine compounds. The data is welcome, though it may herald troubles. Staples reported performance of various metal exchanged zeolites, and a procedure for

regenerating silver zeolite. Critique of his paper centered around economics: The process appears technically sound, but is it really worth the bother? There may be simpler means to make use of the potential inherent in zeolites or other inorganic chemisorbers.

Deitz and Evans gave data on a new variety of impregnated activated carbon. The material appears promising; it can be made from more readily obtainable coal base carbon. It is disappointing that this new material does not have the kind of order-of-magnitude performance improvement that zeolites represent (though at great cost, and same environmental sensitivity).

To overcome these problems, we need adsorption materials which provide penetrations one-tenth to one-hundredth allowable levels, with reliability over the entire range of operating and accident conditions. The materials now available meet regulatory goals, but at the price of painful quality control and monitoring. As we struggle to find how current materials respond to the environments they face, and how to keep them operating <u>at</u> allowable performance levels, we should reserve some effort for materials which advance performance by orders of magnitude, not fractions of a percent.